VALORIZATION OF SECONDARY SLUDGE BY HYDROTHERMAL CARBONIZATION COUPLED WITH ANAEROBIC DIGESTION

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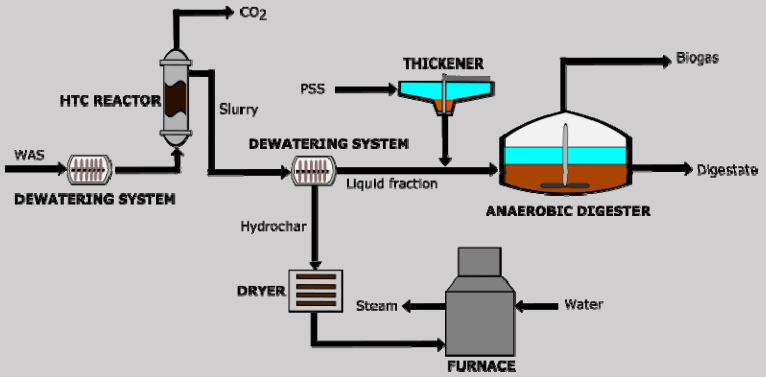

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VALORIZACIÓN DE FANGO SECUNDARIO DE DEPURADORA MEDIANTE CARBONIZACIÓN HIDROTERMAL Y DIGESTIÓN ANAEROBIA

MEMORIA

que para optar al grado de doctor con mención internacional

Presenta

John Alexander Villamil Martínez

Madrid, 2019

Dña. María de los Ángeles de la Rubia, investigadora Ramón y Cajal de la Universidad Autónoma de Madrid y D. Ángel Fernández Mohedano, profesor Titular del Departamento de Ingeniería Química de la Universidad Autónoma de Madrid

HACEN CONSTAR:

que el presente trabajo, titulado: "Valorización de fango secundario de depuradora mediante carbonización hidrotermal y digestión anaerobia", presentado por D. John Alexander Villamil Martínez, ha sido realizado bajo su dirección, en los laboratorios del Departamento de Ingeniería Química, en la Universidad Autónoma de Madrid y que, a su juicio, reúne los requisitos de originalidad y rigor científico necesarios para ser presentado como Tesis Doctoral.

Y para que conste a los efectos oportunos, firmamos el presente informe en Madrid a 24 de abril de 2019

María de los Ángeles de la Rubia Romero Ángel Fernández Mohedano

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Index/Índice

Index

Summary/Resumen

Summary

Hydrothermal carbonization (HTC) is a thermochemical process which converts organic feedstock into a high carbon rich solid product. The process is especially suitable for biomass waste with a high moisture content. This singular advantage of the HTC process eliminates the pre-drying requirement of wet biomass, which is a huge energy intensive process and a financial load in biomass pre-processing especially when performed under conventional thermal pre-treatments like slow-pyrolysis or dry torrefaction.

The management of sewage sludge, in an economically and environmentally acceptable manner, is one of the critical issues facing modern society, due to the very fast increase in sludge production as a result of the implementation of the Directive 1991/271. This is coupled with increased difficulties in complying with legislation on wastes (Directive 1999/31 for landfilling, Directive 2000/76 for incineration). On the other hand, many farmers are reluctant to land utilization of sewage sludge. Therefore, the European Commission has started the development process of a new Directive proposing new severe standards on organic micropollutants and on hygienic requirements.

In this work, the HTC of dewatered waste activated sludge (DWAS) has been studied as a new concept for the management of this waste for producing a renewable solid fuel (hydrochar). Moreover, the potential application of this HTC char as a precursor of activated carbons by using physical or chemical activation has been evaluated. Besides, the HTC process water has been valorized by anaerobic digestion to recovery energy as methane, looking for an approach for implementing the circular economy in the management of sewage sludge.

In Chapter 3, the production of hydrochar using a central composite rotatable design was applied to analyze the effect of temperature (140-220 ºC) and reaction time (0.5-4 h) on the physical and chemical characteristics of hydrochars obtained. BET areas around 25 m^2/g, with a significant mesoporous contribution were obtained at temperatures higher than 180 ºC. The higher heating values (HHV) of hydrochars varied from 19.1 to 22.3 MJ/kg. Air activation (300-450 ºC) showed a decrease of BET area as temperature increased, with values around 100 m^2/g at best. Chemical activation with K_2CO_3, KOH, $FeCl_3$, and $ZnCl_2$ (650 and 850 ºC) provided BET areas in the range from 410 to 1030 m^2/g with an important contribution of meso (0.079-0.271 cm^3/g) and microporosity (0.136-0.398 cm^3/g). The results obtained support the potential application of

hydrothermal carbonization of dewatered waste activated sludge for the production of solid fuel and as a precursor of inexpensive activated carbons with tunable porous structure.

The Chapter 4 is focused on the valorization of the liquid fraction (LF) from HTC of DWAS by batchwise mesophilic anaerobic digestion in batch experiments. On the section 4.1 studies the effect of the initial inoculum concentration (IC; 10 and 25 g COD/L) and the inoculum to substrate ratio (ISR; 0.4, 0.5, 1 and 2 on a COD basis) on the key parameters during the anaerobic digestion, such as pH, alkalinity, volatile fatty acids (VFA), ammoniacal nitrogen, COD and methane potential was studied. LF presented a high organic matter (soluble COD: 95.5 g O_2/L) and nitrogen (TKN: 8.7 g N/L) content. For an ISR below 1 and even at 1 for the highest IC (25 g COD/L) the inhibition of the system occurred, due to the increased availability of easily hydrolysable material in the bioreactor, which in turn led to VFA and TAN accumulation, and consequently a low COD removal was observed. For the experiments with high ISR ratio, the methane yield was in the range 144-177 mL STP CH_4/g COD_{added}, while in the rest of the experiments, the inhibition of the methanogenic stage took place.

The section 4.2 studies the effect of the inoculum source on the anaerobic digestion of the LF from the HTC of DWAS. With this purpose, three inocula sources were compared: a flocculent sludge from an anaerobic digester (MS) treating the sewage sludge of a municipal wastewater treatment plant (MWWTP) and two granular anaerobic sludges from a mesophilic upflow anaerobic sludge blanket (UASB) reactor treating effluents from sugar beets (SB) and from a mesophilic internal circulation reactor treating brewery wastewater (BW). Two inoculum concentration (10 and 25 g COD/L) were tested for each inoculum source, keeping constant the ISR in a value of 2 (on a COD basis). Increasing the IC from 10 to 25 g COD/L the methane production improved by 23% for the BW inoculum (177 mL STP CH_4/g COD_{added}); however a significant decrease was observed for the SB inoculum (99 mL STP CH_4/g COD_{added}). The methane yield (135 mL STP CH_4/g COD_{added}) was not affected in the range of IC tested for the MS inoculum. Thus, the BW inoculum was the most appropriate for the anaerobic digestion of the LF from HTC of DWAS at high IC.

The Chapter 5 studies the anaerobic co-digestion of LF of DWAS with primary sewage sludge (PSS), with the aim to integrate the HTC of DWAS in a wastewater treatment plant. The section 5.1 evaluates this new concept for sewage sludge management by batch

experiments using several mixtures of the LF of DWAS and thickened PSS, as well as the two bare substrates (LF and PSS). Two different inocula (a flocculent sludge from a mesophilic digester of a municipal wastewater treatment plant and a granular one from a brewery wastewater treatment plant) were used. Methane production decreased as the LF/PSS ratio increased, which can be explained by the presence of recalcitrant compounds in the LF, such as alkenes, phenolics, and other oxygen- and nitrogen-bearing aromatics hard-to-degrade through anaerobic digestion. Methane yield reached 248 mL STP CH_4/g COD_{added} with the granular inoculum and a mixture of 25% LF on a COD basis. Beside, the COD was reduced more than 86%, with a negligible concentration of total volatile fatty acids. With both inocula, total Kjeldahl nitrogen hydrolysis increased as the LF to PSS mixture ratio decreased. Methane yield values fitted well the first-order, Cone and Weibull kinetic models for both inocula. Significant differences in the kinetic constant values, in the range 0.100-0.168 d^{-1} and 0.059-0.068 d^{-1}, were found for the flocculent and granular, respectively.

On the section 5.2, the co-digestion of LF from HTC of DWAS was optimized under semi-continuous mode. For this purpose different feed mixture compositions (5% LF and 10% LF, on a COD basis), organic loading rates (OLR; 1.5 and 2.5 g COD/L·d), and temperature regimes (mesophilic (35 ºC) and thermophilic (55 ºC)) were analysed. PSS to LF mixture ratios were chosen according to the results of the batchwise anaerobic co-digestion of PSS and LF, where methanogenesis inhibition was substantial with LF proportions exceeding 25% in the mixture. Under thermophilic conditions, co-digestion of PSS and LF was not feasible, due to the progressive inhibition evidenced by indole accumulation, together with the presence of high concentrations of VFA and NH_3. However, the combination of mesophilic conditions, a 10% LF feed mixture, and OLR of 1.5 g COD/L·d provided a methane yield (172 mL STP CH_4/g COD_{added}), 1.15 times the value for the control test (100% PSS). Therefore, HTC applied to DWAS followed by AD of the LF with PSS enhanced the valorization of this renewable residue. The proposed global treatment allowed obtaining up to 4.4 times more overall energy compared with AD of mixed sludge.

Sewage sludge and the organic fraction of municipal solid waste (OFMSW) are the ones most used as substrate for anaerobic co-digestion. Thus, the Chapter 6 studies the co-digestion of the LF and the OFMSW in batch experiments. The section 6.1 firstly analyzes the effect of pre-treatment (grinding and sieving) on the anaerobic digestion of

OFMSW. Methane yield, after grinding and sieving (20 mm diameter) the OFMSW, was considerably higher (453 mL STP CH_4/g VS_{added}) than that of untreated OFMSW (285 mL STP CH_4/g VS_{added}). The modified Gompertz model adequately predicted process performance. Subsequently, co-digestion experiments were conducted using different mixing ratios of OFMSW (ground+sieved) and LF, on a COD basis. A mixture with 25% LF provided a similar methane yield to that obtained with OFMSW as sole substrate, providing an alternative to manage this process water. The experimental co-digestion results were adequately fitted to a first-order kinetic model, showing a kinetic constant virtually independent of the percentage of LF (0.52–0.56 d^{-1}) in the mixture and decreasing slightly for the experiment with LF as sole substrate (0.44 d^{-1}).

Finally, the section 6.2 includes the co-digestion of LF and OFMSW under thermophilic conditions. Mixtures with a low OFMSW to LF ratio (50, 75 and 100% LF) exhibited accumulation of VFA, as well as low degradation of organic matter and methane production. However, the mixture containing 25% LF performed quite well in terms of methane production, which was only slightly lower than the value obtained with OFMSW as sole substrate. The experimental results fitted the modified Gompertz model reasonably well, achieving the maximum methane production rate for the mixture containing 25% LF (11.96 mL CH_4/g COD·d), which was 29.3% higher than that obtained with the substrate with OFMSW as sole substrate.

Resumen

La carbonización hidrotermal (CHT) es un proceso termoquímico que permite convertir residuos orgánicos en un char con alto contenido en carbono. El proceso se lleva a cabo en presencia de agua, independientemente del contenido en humedad del material de partida. La principal ventaja del proceso CHT radica en poder utilizar el material a carbonizar sin necesidad de un secado previo, lo que requeriría el empleo de gran cantidad de energía, como ocurre en la pirólisis y en la torrefacción.

Actualmente una gestión aceptable de los lodos de EDAR tanto desde el punto de vista económico como ambiental resulta complejo, debido al rápido aumento de producción, como resultado de la implementación de la Directiva 1991/271. Además, se requiere el cumplimiento de la legislación en materia de residuos (Directiva 1999/31 de depósito en vertederos y Directiva 2000/76 de incineración). Por otro lado, muchos agricultores son reacios al empleo de lodos en agricultura y, además, la Comisión Europea ha comenzado el proceso de implementación de nuevas Directivas que recogen normativa en materia de microcontaminantesy requerimientos de higienización de los fangos de depuradora.

En el presente trabajo se estudia la CHT del lodo secundarios de depuradora deshidratados (LSDD) como una nueva vía de gestión de este residuo mediante la producción de un material carbonoso (hidrochar), así como su potencial aplicación como precursor de carbones activos mediante activación física o química. Además, la fracción líquida (agua de proceso) se valoriza mediante digestión anaerobia para recuperar energía en forma de metano, con la intención de implementar la economía circular en la gestión de los lodos de depuradora.

En el Capítulo 3 se estudia la producción de hidrochar, empleando un diseño central compuesto para evaluar el efecto de la temperatura (140-220 ºC) y el tiempo de carbonización (0,5-4 h) sobre las propiedades fisicoquímicas de los hidrochars obtenidos. Mediante CHT se alcanzaron áreas superficiales cercanas a 25 m^2/g, con una importante contribución mesoporosa, empleando temperaturas de carbonización superiores a 180 ºC. El poder calorífico superior se situó en el intervalo 19,1-22,3 MJ/kg, valores ligeramente superiores a los del lignito. En cuanto a la activación con aire (300-450 ºC), el área superficial disminuyó al aumentar la temperatura, alcanzando un valor en torno a 100 m^2/g en el mejor de los casos. La activación química con K_2CO_3, KOH, $FeCl_3$, y $ZnCl_2$, empleando temperaturas de 650 y 850 ºC, permitió el desarrollo de área superficial

en el intervalo entre 410 y 1030 m^2/g, con una significativa contribución de meso (0,079-0,271 cm^3/g) y microporosidad (0,136-0,398 cm^3/g). Los resultados obtenidos respaldan la aplicación de la carbonización hidrotermal de lodo secundario de depuradora como precursor de carbones activados de bajo coste con un importante desarrollo superficial.

El Capítulo 4 se centra en la valorización de la fracción líquida (FL) generada en la CHT de LSDD mediante digestión anaerobia en ensayos en discontinuo. La sección 4.1 estudia el efecto de la concentración inicial de inóculo (CI; 10 y 25 g DQO/L) y la relación inóculo-sustrato (RIS; 0,4, 0,5, 1 y 2 en base a DQO) en las variables más importantes durante el proceso de digestión, como pH, alcalinidad, concentración de ácidos grasos volátiles (AGVs), nitrógeno amoniacal, DQO y potencial de metano. La fracción líquida obtenida en los ensayos de CHT presentó un elevado contenido en materia orgánica (DQO soluble de 95,5 g O_2/L) y nitrógeno total Kjeldahl (NTK de 8,7 g N/L). Para una RIS inferior a 1 e incluso superior en el caso de emplear una CI elevada (25 g DQO/L) se observó la acumulación de AGVs y NTK, unido a una baja producción de metano. En los experimentos realizados con una elevada RIS se obtuvo una producción de metano en el intervalo de 144-177 mLN CH_4/g $DQO_{añadida}$, mientras que el resto de experimentos presentaron inhibición metanogénica.

En la sección 4.2 se estudia el efecto de la fuente de inóculo empleado en la digestión anaerobia de la FL de la CHT de LSDD. Así, se evaluaron tres inóculos de diferente procedencia: un lodo floculento obtenido de un digestor anaerobio de una estación depuradora de aguas residuales (EDAR), un fango granular procedente de un reactor anaerobio de lecho expandido que trata el agua residual de una fábrica de azúcar de remolacha y un reactor anaerobio mesofílico con recirculación interna que trata el agua residual de una fábrica de cerveza. Se analizó el efecto de la CI (10 y 25 g DQO/L), manteniendo para cada inóculo una RIS de 2 (en base a DQO). Al aumentar la CI de 10 a 25 g DQO/L la producción de metano aumentó un 23% en el caso del inóculo procedente de la industria cervecera (177 mLN CH_4/g $DQO_{añadida}$); sin embargo, se observó una disminución significativa al emplear el inóculo obtenido en la fábrica de azúcar (99 mLN CH_4/g $DQO_{añadida}$). La producción de metano se mantuvo constante para el inóculo procedente de la EDAR (135 mLN CH_4/g $COD_{añadida}$) en el intervalo de CI ensayado. Por lo tanto, el inóculo procedente de la fábrica de cerveza resultó el más adecuado para la digestión anaerobia de la FL de la CHT empleando elevadas CI.

En el Capítulo 5 se estudia la codigestión anaerobia de la FL de la CHT de LSDD con fango primario (FP) de depuradora, con el objetivo de integrar la CHT de LSDD en una EDAR. En la sección 5.1 se evalúa este nuevo concepto de gestión de los fangos de depuradora, en ensayos en discontinuo utilizando diferentes proporciones de LSDD y FP, así como ambos sustratos de forma independiente. Los ensayos se realizaron empleando dos inóculos diferentes (un lodo floculento obtenido del digestor de una EDAR y un lodo granular de un reactor anaerobio mesofílico con recirculación interna que trata el agua residual de una fábrica de cerveza). La producción de metano disminuyó al aumentar la relación FL/FP, debido a la presencia de compuestos recalcitrantes en la FL como alquenos, fenoles y compuestos aromáticos nitrogenados y oxigenados difíciles de degradar mediante digestión anaerobia. La producción de metano alcanzó valores de 248 mLN CH_4/g $DQO_{añadida}$ empleando como inóculo el lodo floculento y una mezcla con un 25% FL, lo que supuso un aumento del 74% respecto al ensayo realizado únicamente empleando FL. Además, se consiguió una eliminación de DQO superior al 86%, con una concentración de AGVs despreciable. Para ambos inóculos, la hidrólisis de NTK aumentó al disminuir la relación de FL/FP. Los valores de producción de metano se ajustaron adecuadamente a los modelos cinéticos de primer orden, Cone y Weibull. Se observaron diferencias significativas en los valores de las constantes cinéticas obtenidas en el intervalo 0,100-0,168 d^{-1} y 0,059-0,068 d^{-1} para los inóculos floculento y granular, respectivamente.

En la sección 5.2 se estudia la optimización, mediante ensayos en semicontinuo, de la digestión anaerobia de FL y FP. Se llevaron a cabo ensayos utilizando relaciones de FL de 5 y 10% (en base a DQO), velocidades de carga orgánica de 1,5 y 2,5 g DQO/L·d, y temperaturas en el intervalo mesofílico (35 ºC) y termofílico (55 ºC). En condiciones termofílicas la codigestión de FL y FP no resultó factible, debido a la inhibición progresiva del sistema, que se pudo evidenciar por la acumulación de indol, junto con la presencia de elevadas concentraciones de AGVs y amonio. Sin embargo, la operación en condiciones mesofílicas, empleando una mezcla con un 10% FL y una velocidad de carga de 1,5 g DQO/L·d, permitió obtener una producción de metano (172±11 mL CH_4/g $DQO_{añadida}$), 1,15 veces mayor al control (FP como único sustrato). Por lo tanto, la CHT de lodo secundario deshidratado y la posterior digestión anaerobia de la FL generada permitió la valorización de este residuo renovable. Además, el tratamiento integrado

propuesto permite obtener una producción energética (hidrochar+biogás) 4,4 superior al obtenido con la digestión anaerobia del lodo mixto.

Los lodos de EDAR son actualmente, junto con la fracción orgánica de los residuos urbanos, los dos sustratos más utilizados en procesos de codigestión. Por ello, en el Capítulo 6 se estudia la codigestión de la FL de la CHT de LSDD con FORU, mediante ensayos en discontinuo. En la sección 6.1 se analiza, en primer lugar, el efecto del pretratamiento del FORU, después de operaciones de molienda y tamizado, en la digestión anaerobia de FORU. La producción de metano de FORU después de la molienda y tamizado (diámetro 20 mm) resultó considerablemente mayor (453 mLN CH_4 /g $SV_{añadidos}$) que para el FORU sin pretratar (285 mLN CH_4/g $SV_{añadidos}$). El modelo cinético de Gompertz modificado ajustó adecuadamente la evolución de la producción de metano empleando FORU pretratado. Seguidamente, se realizaron ensayos de codigestión anaerobia de FORU pretratado y FL utilizando diferentes mezclas de ambos sustratos en base a DQO. El rendimiento en metano obtenido para la mezcla con un 25% FL resultó similar al generado empleando únicamente FORU pretratado. Los resultados experimentales de producción de metano se ajustaron adecuadamente a una ecuación de primer orden, obteniéndose valores de la constante cinética en el intervalo 0,52-0,56 d^{-1}, independientemente del porcentaje de FL empleado, y observándose una disminución de estos valores para el experimento realizado únicamente con FL (0,44 d^{-1}).

Finalmente, la sección 6.2 incluye experimentos similares de codigestion de la fracción líquida y FORU realizados en esta ocasión en condiciones termofílicas. Las mezclas con menor contenido en FORU (50, 75% de FL) así como el experimento realizado únicamente con FL mostraron la acumulación de AGVs, así como una reducida degradación de materia orgánica y producción de metano. Sin embargo, la mezcla que contenía un 25% de FL alcanzó una producción de metano ligeramente inferior a la obtenida en el ensayo realizado con FORU pretratado. Los resultados experimentales se ajustaron adecuadamente al modelo de Gompertz modificado, obteniéndose la máxima velocidad de producción de metano empleando la mezcla con un 25% de FL (11,96 mL CH_4/g $DQO_{añadida}$·d), la cual resultó ser un 29,3% superior a la obtenida empleando únicamente FORU pretratado.

Chapter 1:

Introduction

1.1. Hydrothermal carbonization of biomass waste

Biomass waste can be valorized by means of well-stablished thermochemical processes such as pyrolysis, dry torrefaction and gasification. Pyrolysis promotes the chemical decomposition of biomass at temperatures within the range 300–650 ºC in the absence of oxygen. The process results in the formation of a carbon-rich solid product, called biochar, a volatile matter which can be partially condensed to liquid phase (bio-oil), and a gaseous phase, which usually includes CO, CO_2, CH_4, and H_2 [1]. Dry torrefaction is a mild pyrolysis process carried out in an inert atmosphere at temperatures of 200–300 ºC and a residence time of ≈ 0.5-2 h. This process has gained interest for improving the physicochemical properties of biomass for combustion, since the specific energy density of the torrefied solid product is increased, with very low mass loss (≅ 30%) and gas production (10%). Finally, biomass can be partially combusted via gasification at very high temperatures (600–1200 ºC) for a very short residence time (10–20 s), obtaining a mixture of gases (CO, H_2, and CO_2), usually named Syngas, and ash [3].

Hydrothermal carbonization (HTC) was firstly described by Friedrich Bergius in 1913 to describe the natural coalification process. Although the process did not gain attention until the last decades 20th century as a method to obtain organic compounds for the synthesis of chemicals along with the recovery of liquid and fuels. Recently, it has been rediscovered for the production of hydrochar, which has value-added applications in the industry and environment [2]. Actually, and due to the growing interest in this technology, the 1st and 2nd International Symposium on Hydrothermal Carbonization have been celebrated in London (2017) and Berlin (2019), respectively.

Table 1.1. Characteristics of the main thermochemical processes for biomass conversion.

		Pyrolysis	**Gasification**	**Hydrothermal carbonization**
Temperature (ºC)		300-650	600-900	180-300
Time		5 min-24 h	10-20 s	5 min-24 h
Mass yield (%)	**Solid**	25-35	<10	45-70
	Liquid	20-30	<5	5-25
	Gas	25-35	>85	5-25

HTC is a thermochemical process for the treatment of high moisture content biomass, which is performed in a wide range of temperature (180-350 ºC) and autogenous pressure (2-6 MPa) for variable periode of time (5 min-24 h) [4,5]. Under these conditions, the

water acts as an ideal solvent for extraction. Moreover, as the temperature and pressure increase, the surface tension, dielectric constant and viscosity increase too, while the diffusion rate decreases [6].

The main products of HTC process are a solid (hydrochar), a liquid fraction (also referred as HTC liquor or HTC process water (PW)), which could contain up to 15% of the initial carbon present in the feedstock [7], and a gas phase mainly formed by CO_2 (>90%) and a small amounts of CH_4, H_2, and CO [8,9]. Usually, moderate temperatures promote liquid yield, whereas higher temperatures generate gas and char, mainly. Table 1.1 shows the characteristics of the main thermochemical processes for biomass conversion.

The *carbonization temperature* is the key variable in HTC process [10], having great influence on the chemical composition [11], morphology [12], and energy content [7] of the hydrochar and the carbon and nitrogen contents [13] and pH [14] of the aqueous phase. Falco et al. [15] and Jamari and Howse [16] observed an increase in the hydrochar carbon content with the temperature, related with the biomass dehydration. Although, a higher temperature increase can cause a hydrochar yield decrease, due to gasification [17,18]. However, Hoekman et al. [19] reported an increase of the hydrochar yield at higher temperature, as a consequence of the condensation and dehydration reactions and the formation of polymers. The morphology of hydrochar is affected by temperature as well. In this way, Sevilla and Fuertes [20] obtained a hydrochar from cellulose carbonized at 210 ºC with an irregular morphology similar to feedstock, whereas at 220 ºC aggregates of microspheres (2-10 μm) were observed.

The *reaction time* also has an important role in the HTC process. Lu et al. [21] determined an increase in the hydrochar carbon content of cellulose as the reaction time. Long-term HTC experiments show a decrease in hydrochar yield due to the polymerization of monomers and solved fragments in the aqueous phase [19,22] and transference of carbon to the gas phase (around 7-9% of carbon content, mainly as carbon dioxide, butane, furan, ethylene, ethane, and propane in trace amounts). The hydrochar morphology is also affected by reaction time. Romero-Anaya et al. [23] obtained spherical carbons after long carbonization time of carbohydrates (12-24 h). Similar results were reported by Gao et al. [24], who observed an increase in the number of microspheres increasing the reaction time of water hyacinth.

In general, high *heating rate* exerts a negative impact on hydrochar yield. Brand et al. [25] determined a decrease of hydrochar yield on the carbonization of red pine sawdust and cellulose at subcritical condition (250-300 ºC), after increasing the heating rate from 2 to 20 ºC/min. However, for low heating rate, the increase of temperature and reaction time resulted in a high degree of carbonization, related with the decrease of O/C and H/C atomic ratios. Therefore, high heating rates decrease the higher heating value (HHV) [22].

HTC have been applied to a great variety of lignocellulosic biomass, with variable composition in hemicellulose (20-40%), cellulose (40-60%) and lignin (10-25%), and to non-lignocellulosic ones, such as animal manure, food, sewage sludge and municipal solid wastes, among others, which have significant different composition. The most important advantages of this technology are:

(1) No previous waste drying requirement.
(2) Reduction of waste volume to landfill (90-95%) [26].
(3) High stability of treated feedstock.
(4) Improvement of cost-effectiveness compared to conventional thermal drying.
(5) Obtaining a hydrochar with high energy density.
(6) Decrease of nitrogen content up to 50%, reducing NO_x emission compared with the feedstock combustion [27–29].
(7) Efficient pelletization compared to biochars, diminishing transport cost and handling difficulties [30].
(8) Improvement of surface properties of hydrochar by chemical activation [31,32].

1.2. Applications of hydrochars

HTC technology is gaining attention for the potential applications of hydrochar on different fields, including soil amendment, water purification, energy storage, CO_2 sequestration, and catalysis, among others.

Solid fuel

The hydrochar is a carbon-rich and energy-dense material that offers enormous potential as a solid fuel from a renewable source for energy valorization. Hydrochar has several advantages against another coal and carbonaceous material obtained by thermal treatments including pyrolysis, activation, among others. First of all, HHV relatively high (<31 MJ/kg) and close to low-rank brown coal and lignite, can be reached at relatively low temperatures (180-250 ºC), improving the energy-efficient treatment [32]. Secondly,

a significant environmental benefit associated with reducing of pollutant emission can be achieved, thanks to the lower nitrogen and sulfur content of hydrochar compared with conventional chars obtained from activation and pyrolysis. Hydrochar energy content is affected by biomass carbon and hydrogen contents, being also sensitive to biomass ash content, feedstock oxygen content, temperature, and reaction time [33]. It must be taken into account that the increases in biomass ash content (inorganic fraction) decrease the hydrochar energy content.

Soil amendment

Biochar is usually produced with the aim to be applied to soil, to improve its health by filtering and retaining nutrients from percolating soil water, and providing carbon storage. HTC process can be used to produce a hydrochar, with very similar characteristic of biochar, using as a feedstock a variety of nontraditional sources: wet animal manures, human waste, sewage sludge, municipal solid waste (MSW), as well as aquaculture and algal residues [34]. Rillig et al. [35] tested the effect of beetroot chip-derived HTC material on plant growth, finding that increasing concentrations of hydrochar could be deleterious for plant growth of *Taraxacum*. These results suggest that hydrochar should be carefully tested and optimized to avoid negative effects on plant growth.

Adsorbent

Hydrochar has a small surface area, with low pore development and a negative surface charge due to surface polar functional groups [36]. BET surface areas of hydrochars around 30 m^2/g have been obtained by nitrogen adsorption isotherms [10]. These low BET values could be explained for the migration of organic compounds from the aqueous phase to the hydrochar surface, blocking the access to the pores [37]. Hydrochars from waste including sugarcane bagasse, bamboo sawdust, corn digestate, swine solids, poultry litter, oak wood, anaerobically digested waste, or treated municipal waste have been applied as adsorbent for pollutants removal such as herbicides, pharmaceuticals, personal care products, and heavy metals. Hydrochars from swine solids and poultry litter exhibited relatively low effectiveness in removing cadmium (II) [38], due to variable negative charges on their surface, being more negative at high pH, affecting the electrostatic attraction between the hydrochar and the metal.

The small surface area and pore volume development of hydrochars limit its use as adsorbents. This lack can be overcome by physical or chemical activation for textural properties development. In this regard, hydrochars have received increasing attention as

precursors of activated carbons thanks to their low condensation degree, which can be fitted to produce activated carbons with tunable surface properties, e.g., high concentration of oxygenated functional groups, which act as active sites interacting with and immobilizing other molecules [31,39]. Various chemical: KOH, NaOH, H_3PO_4, H_2O_2 and, physical: CO_2 and air activating agent have been successfully applied, increasing substantially the BET area. Romero-Anaya et al. [23] reached surface areas up to 3150 m^2/g for HTC (200 ºC-24 h) of glucose and subsequent chemical activation (750 ºC-1 h) with KOH. However, physical activation with CO_2 generated a lower content of surface oxygen groups than chemical one.

1.3. Sewage sludge as feedstock for HTC process

Sewage sludge (SS) represents the major solid waste derived from municipal wastewater treatment plants, and includes high organic matter content, macro (phosphorus, nitrogen), and micronutrients (Al, Fe, K, Ca, among others), trace organic contaminants, and pathogenic organisms. Sludge can be categorized, depending on the wastewater treatment stage in the wastewater handling units, as primary sludge (produced during primary wastewater settlings), secondary or waste activated sludge (produced during secondary biological treatments), mixed sludge (primary and secondary sludge mixtures), and tertiary sludge (produced during tertiary or advanced wastewater treatments). The sludge can be further processed in the sludge treatment-line, where it can be stabilized by means of digestion processes (digested sludge) and dewatered by means of solid/liquid separation systems (dewatered sludge) [40].

Sewage biosolids are mainly composed of lignin (15-30%), proteins (40%), lipids (10-25%), carbohydrates (14%) and ash, which can be decomposed by hydrothermal carbonization to alcohols, aldehydes, carboxylic acids, amino acids, fatty acids, and furfurals [4]. Fig. 1.1. shows the main organic components in sewage sludge and their hydrolysis products under HTC process.

Fig. 1.2. depicts the schematic hydrochar formation from HTC of sewage sludge. Under hydrothermal conditions, different reaction ways take place due to the presence of saccharides and proteins or amino acids. The amino acid degradation can be affected by a low pH that is caused by the conversion of saccharides. Therefore, the pH plays a crucial role over amino acid treated hydrothermally. Abdelmoez et al. [41] studied the amino acid transformation and decomposition under subcritical condition (230-290 ºC) and reported that the ones most stable were found at high pH value (ionized form) while a

reverse trend was observed at near neutral and acidic pH value. These results also have shown that glycine and valine were very stable, whereas cysteine and glutamic acid exhibited an opposite trend. During HTC process, Maillard reaction is carried out between the carbonyl group of sugar with the amine group of the amino acid, to obtain polymeric compounds named melanoidins. This reaction is responsible for the typical odor and brown color of sewage sludge hydrochar.

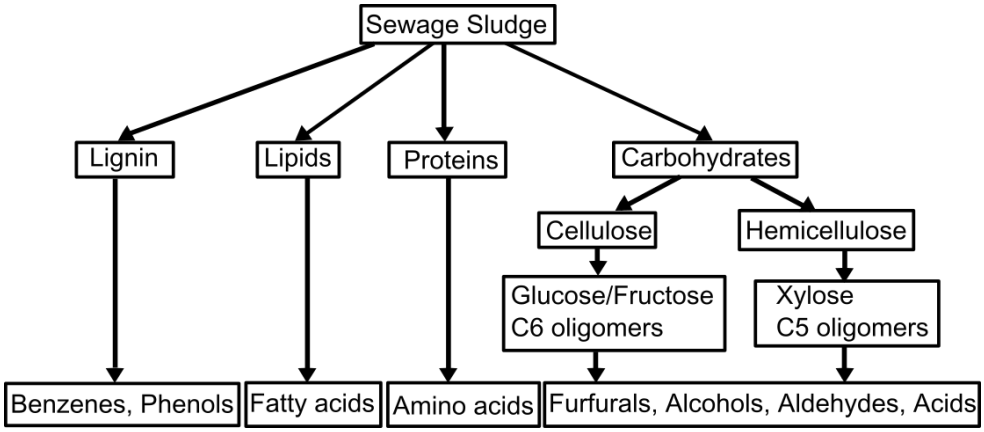


Fig. 1.1. Main organic components in sewage sludge and their products under hydrothermal condition (modified from He et al. [4]).

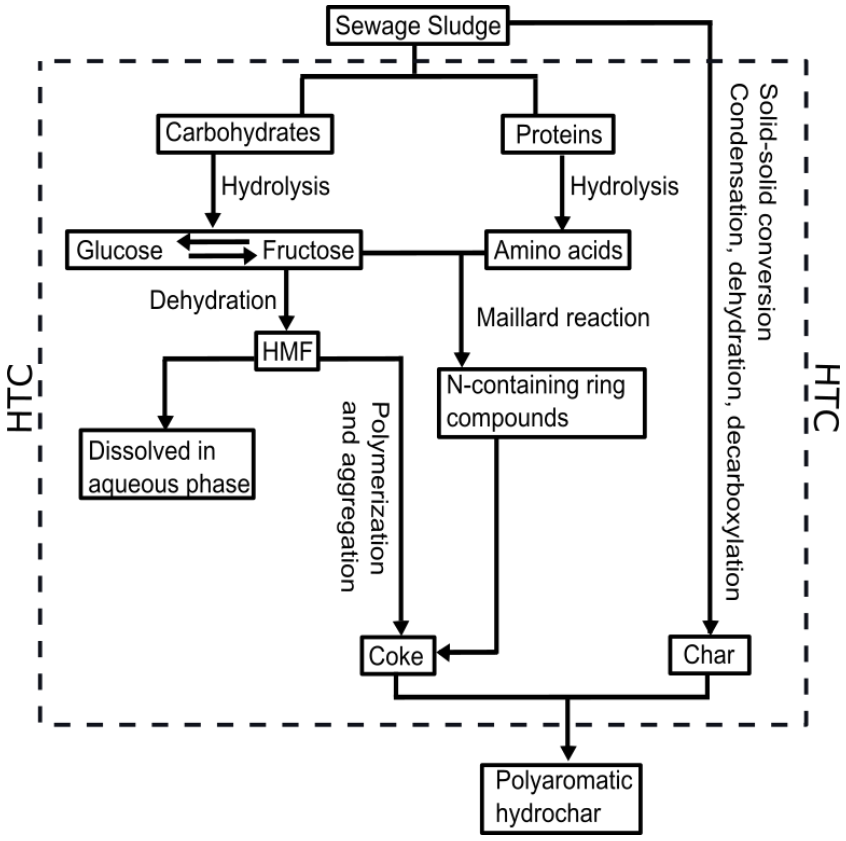
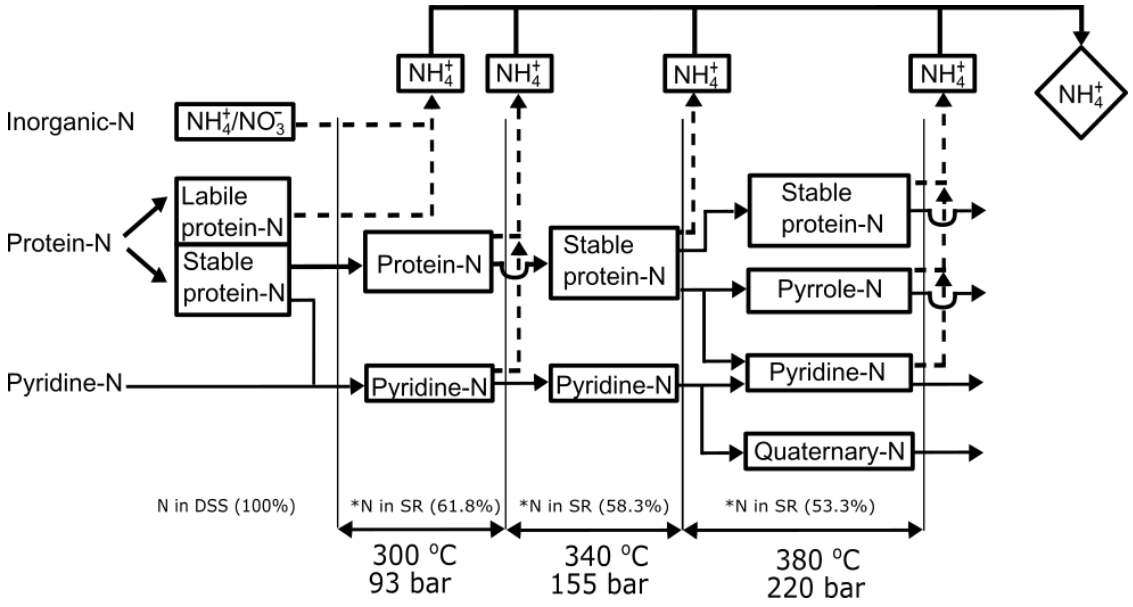


Fig. 1.2. Schematic sewage sludge-derived hydrochar formation mechanism under hydrothermal conditions (modified from He et al. [42]).

Nitrogen-containing aromatic compounds and amines were found in the aqueous phase as a result of Maillard reactions, whereas in hydrochar heterocyclic nitrogen compounds including quaternary–N and pyridine-N have been found. Danso-Boateng et al. [7] found different Maillard compounds such as aldehydes, furans, pyrroles, pyrazines, and pyridines from HTC of primary sewage sludge (4.3%, wt.) at temperatures and reaction times higher than 180 ºC and 15 min, respectively. Inoue et al. [43] observed (after HTC of dewatered sewage sludge) transferences of N-content from sewage sludge to the aqueous phase higher than 60%. Moreover, the solubilization and decomposition of N-content were promoted as well. Fig. 1.3. shows the possible nitrogen pathway of dewatered sewage sludge under different hydrothermal conditions. The deamination reaction presented three main hydrothermal states. Firstly, most the ammonium (NH_4^+-N) was released at temperatures <300 ºC (93 bar) from deamination of labile protein-N as well as the hydrolysis of inorganic-N substances [13]. Secondly, a significant nitrogen removal is due to meaningful deamination of pyridine-N compounds in the temperature range of 300-340 ºC with the pressure of 93 and 155 bar, respectively. Meanwhile, the production of quaternary-N compounds by the pyridine-N intermediates were also observed. Last, the raising of content pyrrole-N and pyridine-N could be as a result of deamination of stable protein-N at temperatures >380 ºC (220 bar).

Most remarkably, the quaternary-N compounds were completely converted to pyridine-N compounds. Most studies in HTC of sewage sludge are focused on obtaining hydrochar as renewable biofuel [7,27,42,44–46]. Some authors have paid attention to the recovery of nutrients [14,47], pharmaceuticals [48], and heavy metals in the products streams. Even, the use of hydrochar as adsorbent [49,50] and soil improver [7,51] has been evaluated.



(*%N in the solid residue (SR): amount of nitrogen in the resulting material after hydrothermal treatment).

Fig. 1.3. Possible nitrogen pathway of dewatered sewage sludge (DSS) hydrothermally treated. (modified from He et al. [13]).

Table 1.2. summarized the operational conditions and main characteristics of the hydrochars obtained from HTC of sewage biosolids. One of the main disadvantages of the HTC materials, including sewage sludge hydrochars, is that they present limited porosity and surface area [45,49,50]. N_2 adsorption is not a proper method to characterize the textural properties of hydrochar since they only present ultramicropores (<0.5 nm). Thus, CO_2 adsorption isotherm could be a better option [34].

Table 1.2. Main characteristics of the hydrochars obtained from HTC of sewage sludge under typical operational conditions.

Feedstock	Solid (%)	Temperature (ºC)	Time (min)	Solid yield (%)	C (%, wt.)	HHV (KJ/kg)	Reference
Dewatered sewage sludge	20.1	190-220	300-420	60.2	25.9-41.1	11.02-19.1	[52]
Secondary sewage sludge	10	250	15	-	40.1	15.8	[45]
Digested sewage sludge	14.3	200	240-720	60.4	33.0	14.7-15.1	[42]
Dewatered sewage sludge	12.0	200	30	-	41.9	-	[29]
Sewage sludge digested	3.6	180-280	30	80.4-93.9	40.0-48.4	16.5-22.4	[44]
Municipal sludge	20.0	190-260	60-1440	-	35.9-38.6	16.7-18.3	[53]
Dewatered activated sludge	14.0	180-240	15-45	-	52.2-67.9	18.8-20.2	[27]
Primary sewage sludge	4.3	140-200	15-240	60.5-81.1	37.2-39.2	17.0-19.0	[7]
Sewage sludge	10.7	180-300	30-480	53.0-66.2	19.6-24.5	11.0-12.1	[46]
Dewatered biological sludge	14.4	120-210	60	43.4-93.7	35.1	22.7-28.2	[54]
Dewatered sewage sludge	17.5	200-300	20	-	39.9	-	[55]
Secondary sewage sludge	11.0	270	120	-	-	-	[56]
Dewatered sewage sludge	10.7	220-300	60	48.2-57.7	22.3-23.2	9.6-10.3	[57]
Sewage sludge	-	180-200	240-480	-	57.3-58.6	-	[51]
Digested sewage sludge	19.0	200	30	65.0-85.0	23.4	-	[28]
Dewatered sewage sludge	14.4	120-210	60	-	30.2-36.6	22.7-27.0	[58]
Digested sewage sludge	19.0	200	30	-	23.3	-	[59]

1.3.1. HTC process water from hydrothermal carbonization

Depending on the process conditions, the HTC liquor can contain up to 15-20% of the initial carbon, mainly in the form of formic and acetic acids, sugars, nutrients and other compounds [60,61]. Also, the formation of recalcitrant or inhibitory compounds such as furfural, phenols and furan may occur during the HTC process [62,63]. Therefore, that liquid fraction has much higher total chemical oxygen demand (TCOD) than most organic wastewaters. Besides, the HTC conditions (temperature and time) affect TCOD. Values around 60 g/L have been reported from HTC of food waste or orange pomace [64,65] and somewhat lower values (40-50 g/L) have been obtained from agro-industrial residues like chaff, corn silage or thin stillage [66,67], while for HTC of sewage sludge (primary, mixed or digestate), values of 23, 52.5 and 34 g/L, have been reported, respectively [68,69]. Therefore, the liquid fraction from HTC, needs to be conveniently managed before final discharge and moreover its high organic load offers potential interest for the sake of valorization. Different solutions have been proposed, including the use as feedstock for chemical production [70] recycling in consecutive HTC runs to improve the carbon yield or biological stabilization [61,71]. Chemical and biological treatments have been evaluated for the liquid fraction from HTC of sewage sludge. Wet air oxidation allowed reducing total organic carbon (TOC) up to 60% [72]. Ramke et al. [73] obtained a COD reduction over 85% upon aerobic degradation. Anaerobic digestion of that liquid fraction has been suggested as a potential route to optimize energy recovery [74,75]. HTC process water from sewage sludge contains high concentrations of organic matter, characterized by high TOC (in the range of 3.7-62 g/L), and COD concentrations (in the range of 12.7-64 g/L) and relatively abundance of nutrients (N, P, K) (Table 1.3.). These characteristics allows its valorization through the anaerobic digestion (AD) [67–69,76–78]. Macro- and micro-nutrients are generally present to a sufficient extent in the process water from HTC of sewage sludge satisfying the nutrient requirements of anaerobic microorganims. Nevertheless, carbonization at high temperature generates phenolic and furanic compounds [79], high nitrogen amount with nitrogen-containing species which showed different resistances and inhibitory effects to anaerobic degradation [40].

Table 1.3. Main characteristics of the process water from the HTC of different waste.

Feedstock	Solid (%)	T (ºC)	t (min)	Energy yield (%)	COD (g/L)	TOC (g/L)	Nitrogen (g N/L)	CH_4 yield	Comments	Reference
Municipal sewage sludge	10	170-190	10-60	-	30.0-52.5	11.3-22.4	2.3-3.4 (g/L TN)	350 mL CH_4/g COD aqueous phase	COD removal up to 73.3% was reached	[68]
(1) Cow manure (2) Pig manure (3) Sewage sludge (4) Fruit/vegetable waste (5) Food waste	(1) 34.7 (2) 6.9 (3) 7.2 (4) 4.1 (5) 4.4	170	60	-	(1) 30, (2) 43.8, (3) 30.0, (4) 48.6, (5) 134.0	(1) 11.7 (2) 18.9 (3) 9.3 (4) 13.7 (5) 59.1	(1) 1.6 (2) 3.8 (3) 1.7 (4) 1.8 (5) 3.1	(1) 140 mL CH_4/g VS (2) 291 mL CH_4/g VS (3) 257 mL CH_4/g VS (4) 326 mL CH_4/g VS (5) 491 mL CH_4/g VS	The biodegradation of biomass waste were improved except for food waste and cow manure	[78]
Mixture of corn silage and digestate	15	180	240	69-84	-	13-26	-	6.0-16.3 mL/g fresh matter	The methane yield increase as TOC increase in the aqueous phase	[80]
Corn silage	-	220	360	-	41.4	15.7	229 mg/L NH_4-N 685.5 mg/L TKN	163-236 mL CH_4/g COD for CSTR 178-219 mL CH_4/g COD for anaerobic filter	COD removal up to 75% was reached	[67]
Thin stilage	10-14	200-240	30-120	4.0	50.1	-	-	~ 340 mL CH_4/g COD	COD removal higher than 91% was reached	[81]
Brewer's spent grain	23.5	200-240	840	62	60.8-64.2	14 g DOC/L	-	287-405 mL CH_4/g VS	Benzenediols, phenols and fatty acids were formed	[82]
Digestate	10	230	360	-	13.9-20.6 g/kg	1.4-1.8 g/kg	1.6-6.6 g/kg (TAN)	3.4 mL/g hydrochar (d.b.); 52.7% CH_4	Digestate hydrochar increased the CH_4 production by 32%	[83]
Commercial unbleached tissue paper	9.1	200	960	71.6-88.7	24.8-47.9	9.2-15.3	-	344-477 mL/g organic dry matter	The methane production was not increased by reuse of process water	[84]
Pomace	11	175-260	30-120	-	49-69	16-25	-	195-213 mL CH_4/g COD	Methane yields decreased as temperature increased	[65]
Cellulose	10	250	360	-	-	4.0-4.3	5 g/kg TAN	80-110 mL CH_4/ g feeedstock	NH_4-N content provoked inhibition of methanogenesis	[85]
Primary sewage sludge	4.3	140-200	15-240	75-88	17.5-23.0	4.9-13.7	1.0-1.3 (TAN)	31.7-77.4% CH_4	Theoretical methane yield of process water according to correlation of Franco et al. [86]	[7]
Digestate	4.5	160-250	30	61-70	12.1-13.0	4.6-4.9	2.1-2.4 (TKN)	226-277 mL CH_4/g COD	BMP values for process water	[76]
Spent coffee ground	39.3	180-250	60	85-91%	-	-	-	367-491 mL CH_4/g VS	BMP values for process water	[77]

1.3.2. Nutrient recovery from HTC products

Hydrothermal technology continues gaining attention for nutrient recovery, especially from manure and sewage sludge, with high phosphorous and nitrogen contents [6]. Idowu et al. [87] pointed out that most calcium, magnesium, and nitrogen remain in the hydrochar while most sodium and potassium were present in the aqueous phase. Ekpo et al. [14] studied the pH effect on nitrogen and phosphorous extraction, using NaOH, H_2SO_4, CHOOH, and CH_3COOH (all of them 0.1 M) by thermal hydrolysis (120-170 ºC, 1 h) and HTC (200-250 ºC, 1 h) of swine manure. Temperature was determinant in phosphorous extraction to the process water, achieving the highest recovery with H_2SO_4 at 170 ºC; however, phosphorous was mostly retained in the hydrochar. H_2SO_4 was also the best option for nitrogen recovery. These results have been endorsed by Zhao et al. [88]. Aragón-Briceño et al. [76] reported increases in aqueous phase from 3 to 14% of total soluble phosphorus concentration and TKN values from 2066 to 2354 mg N/L, when the HTC temperature of digested sludge increased from 160 to 250 ºC. The recovery of phosphate from the process water from HTC of sewage sludge can be got by precipitation of struvite with $MgCl_2$. Munir et al. [26] improved the abovementioned results by increasing pH and magnesium ion dose.

1.4. Anaerobic digestion

Anaerobic digestion (AD) is a versatile and inexpensive process that allows recovering the energy contained in organic residues in the form of hydrogen and/or methane. The final product of anaerobic digestion is biogas, a gas mixture constituted essentially of two gases (CH_4 and CO_2), where C atoms exhibits the maximum difference in their oxidation state: +4 in the CO_2 the most oxidized state, whereas -4 in CH_4 totally reduced [89]. Biogas can be used for heating, co-generation of electricity or being upgraded to natural gas. The production of biogas requires the presence of consortia of microorganisms whose actions are linked.

Hydrolysis. During the first step of this biochemical process, as can be seen in Fig. 1.4., hydrolytic bacteria, mainly belong to *Bacteroidetes* and *Firmicutes* phila [90], breakdown complex organics proteins, fats, carbohydrates, and some other biodegradable polymers, into monomers such as amino acids, glycerols, fatty acids, and simple sugars, catalyzed by extracellular enzymes such as cellulases, proteases, and lipases [91].

Acidogenesis. During the acidogenesis, fermentative acidogenic bacteria convert products of hydrolysis to intermediary products such as volatile fatty acids (VFAs) (formic, acetic, propionic, butyric, valeric), other products (lactic and succinic acids, alcohols and ketones), and gases as carbon dioxide, and hydrogen; being acetate the major product of carbohydrate fermentation. This fast step can lead to VFA accumulation. *Acetogenesis:* acetate, formate, H_2/CO_2, and methyl compounds are metabolites for methanogens directly. However, butyrate, propionate, lactate, and ethanol need to be further biodegraded during acetogenic phase into acetate.

Methanogenesis. During the methanogenesis stage, acetoclastic, hydrogenotrophic, and methylotrophic *Archaea*, converts the metabolites generated during previous stages in biomethane. Acetate, the main substrate for producing CH_4, can be converted directly by acetoclastic methanogens. This is the pathway for the 70% of CH_4 produced from wastewater [90]. Hydrogenotrophic methanogens also reduce CO_2 to CH_4 using H_2 or formate, therefore these microorganisms are critical for AD process owing to their ability to scavenge H_2 and maintain the pH_2 low [92]. Methylotrophic methanogens metabolize methyl compounds (methanol, methylamines, and methylsulfides) to produce CH_4, although in a small amount. Acetoclastic methanogens belong to two genera: *Methanosaeta*, and *Methanosarcina,* obligate and facultative acetoclastic methanogens, respectively; therefore, most of them can use H_2/CO_2, and methyl compounds in addition to acetate [93]. In general, the most abundant genus of methanogens found in anaerobic digesters is *Methanosarcina* [94]. Among all the phases, the methanogenesis requires a narrower pH range, strictly anaerobic conditions (redox<-330 mV) and micronutrients (Ni, Co, Mo, and Se) [73].

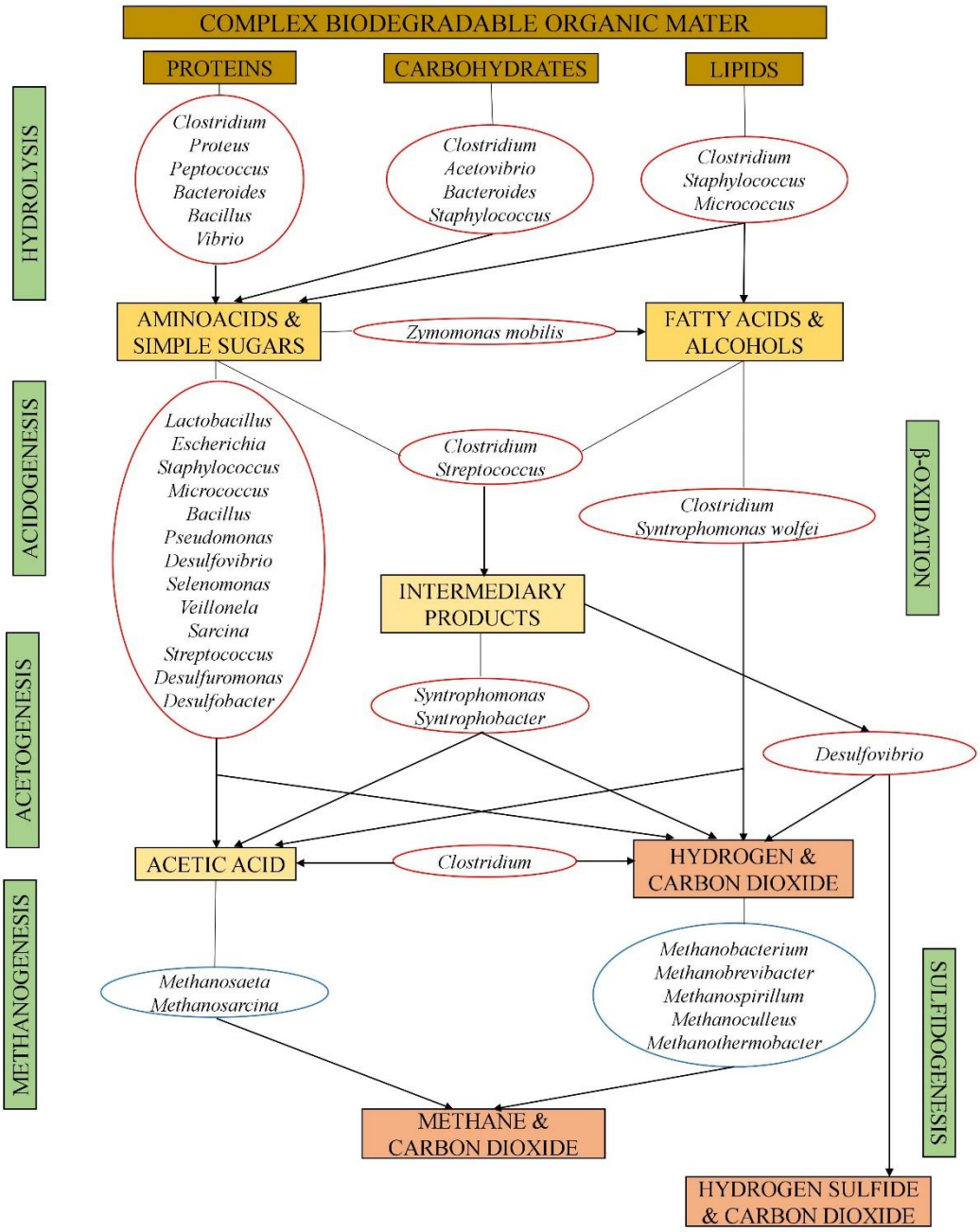


Fig. 1.4. Stages and microorganisms involved in the anaerobic digestion of organic compounds to produce hydrogen and methane (modified from Diaz, [95]).

Factors influencing the anaerobic digestion

Several environmental factors influence the anaerobic digestion: temperature, pH, substrate composition —fat, carbohydrate, and protein contents—, ammonia, heavy metals, organic compounds (chlorophenols, N-substituted aromatics), among others.

The *pH* is an indicator of adequate environment for the microorganisms and plays a critical role in the anaerobic digestion taking into account that this affects the enzymatic reactions [96]. Many studies have reported pH values in the range from 6.8-7.2 for maximum methane production [97–100]. Yao et al. [101] observed that optimal pH for the methanogenic organisms is close to 7.0. While acidogenic microorganisms are favored under acidic conditions (5.5-6.5) [102–104]. *Temperature* is a crucial variable for the microorganism and its adequate selection can enhance their growth. Anaerobic digestion is usually performed in the range from 25-55 ºC. There are three regimens well differentiate where AD is possible. Mesophilic regime (25-42 ºC) promotes a variety of microorganism, which favors the stability of the process compared with the thermophilic one. While the thermophilic range (>50 ºC) compared with mesophilic one is characterized by a lower liquid viscosity, a higher solubility of the organic compounds, higher pathogen deactivation, lower odor emission, faster rate of digestion and consequently shorter retention times [99,105]. However, poor stability associated with elevated ammonia concentrations has been observed [106]. Values in the range from 560-568 mg NH_3-N/L may cause a 50% inhibition of the methanogenesis at pH 7.6 [100,107]. Furthermore, more energy is required and the process control is more difficult [99]. AD is also feasible under the psychrophilic regime (<25 ºC) but at lower rate. In general, it has been reported that the immobilization of anaerobic microorganisms can result in a higher rate of digestion [105].

Ammonia inhibition depends on several factors including temperature, pH, and inoculum adaptation. Excess of ammonia concentration can affect severely to microorganisms growth. The ammonia equilibrium is described as follows:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \quad \text{Eq. 1.1}$$

The non-ionized form (NH_3) or free ammonia nitrogen (FAN) is more toxic for microorganism than NH_4^+ because can diffuse across the membrane. FAN level values inhibit in the range 570-900 mg N/L could inhibit methanogens [108,109]. On the other hand, the ionized ammonia form (NH_4^+) can be inhibitory at levels higher than 5 g NH_4^+/L [110].

The *carbon to nitrogen ratio* (C:N) has a significant impact on anaerobic digestion. Low C:N implies a protein-rich substrate, resulting in increasing nitrogen content by FAN release. In contrast, great C:N can cause a high amount of volatile fatty acids. Optima

C:N between 20 and 30 are usually accepted for adequate anaerobic digestion. The co-digestion has been widely used for nutrients adjustment and to reach optima ratios. C:N of different feedstocks are listed in Table 1.4. (adapted from Siddique et al. [98] and Guillaume and Lendormi [111]).

Table 1.4. Carbon to nitrogen ratio (% wt.) of different biowastes.

Low C:N substrates	**C:N**	**High C:N substrates**	**C:N**
Sewage sludge	6-16	Rice straw	50-68
Cattle manure	15-26	Wheat straw	51-151
Poultry manure	4-16	Sugar cane waste	139-151
Pig manure	7-15	Corn waste	51-57
Sheep manure	20-34	Oats straw	47-51
Horse dung	19-26	Algae	74-101
Kitchen waste	26-30	Sawdust	199-501
Food waste	2-18	-	-

Hydraulic retention time (HRT) and *solid retention time (SRT)* are critical parameters for biological treatment. HRT indicates the time that liquid is held in the digester in contact with biomass (microorganisms). Depending on the complexity of waste, for instance, oxygenated aromatics and chlorinated organic compounds, higher HRT is needed [112]. Meanwhile, SRT is the average time that the biomass is in the digester, controlling the degree of biowaste stabilization, the volatile solid destruction, and consequently the methane production. High SRT values allow a stable treatment, avoiding overloads. Higher SRT than the minimum (SRT_{min}) should be applied to enhance the biological conversion capacity [113]. The equation 1.2 determines the SRT_{min}:

$$SRT_{min} = \frac{1}{Y \cdot \mathrm{k} - b} \quad \text{Eq. 1.2}$$

being Y the biomass growth yield, k the maximum utilization substrate rate, and b the microbial decay rate. In this way, the methanogenic *Archaea* are characterized for low duplication rates, with SRT_{min} of 10 days for mesophilic range, while for psycrophilic range SRT_{min} should be higher than 30 days [112]. For high-rate digestion, SRT_{min} values between 15-20 d are typically used [114].

Several *organic compounds* can inhibit the anaerobic digestion including alkyl phenols, alkanes, halogenated benzenes, phenol, pyridine, and its derivatives, etc. The grade of inhibition depends on various factors such as inocula acclimation, biomass concentration, pollutant concentration, exposure time, feeding pattern, temperature, among others

[115,116]. For example, N-substituted aromatics exert an adverse effect in the anaerobic digestion due to chemical interactions with enzymes, affecting the metabolic pathways [115]. High degree of nitroaromatic inhibition has been reported with values of the IC_{50} in the range of 0.014-0.12 mM [115,117], while aromatic amines resulted less toxic (3.5-67 mM) [115]. The combination of amino and nitro groups, for instance, nitroanilines, resulted in the most toxic compounds. Chen et al. [115] reported that lignin derivatives with apolar substituents or aldehyde groups show high toxicity to methanogenic *Archaea*, whereas inhibition by phenolic acids occurs at very high concentrations.

1.4.1. Anaerobic digestion of sewage sludge

Sewage sludge is a biogenic residue resulting from wastewater treatment process that must be managed properly to circumvent the adverse effects on human health and environment. In general, a WWTP is divided into three main sub-treatment (Fig. 1.5):

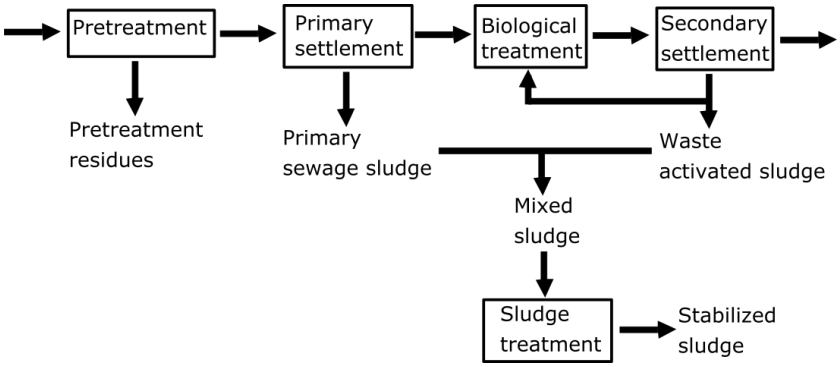


Fig. 1.5. Scheme of sludge generation in a WWTP.

The main goal of preliminary treatment is the removal of grit and coarse solid (sand, plastics, fibers, inert material) using screens and grit chambers. The primary treatment aims to remove partially the suspended solid by several treatment operations such as flotation and sedimentation, producing a by-product called primary sewage sludge (PSS). In the secondary treatment the organic matter is removed by biological treatment, generating a residue named waste activated sludge (WAS). The main characteristics of PSS and WAS are summarized in Table 1.5. WAS is composed by biodegradable organic matter (59-88%), carbon (50-55%), and nitrogen content (10-15%) [119,120] as well as a lower ash content (ca. 20%) compared with PSS (ca. 30%) [121]. On the other hand, WAS shows poor digestibility compared to PSS. After thickening (i.e., dissolved air flotation unit, gravity thickener), the biosolids (WAS and PSS) are mixed and stabilized.

Table 1.5. Representative analysis of primary sewage sludge (PSS) and waste activated sludge (WAS) (adapted from Tyagi et al. [120] and Tchobanoglous et al. [114]).

Parameter	PSS	WAS
Total dry solids (total solids, % TS)	5-9	0.8-1.2
Volatile solids, VS (% TS)	60-80	59-68
Nitrogen (% TS)	1.5-4	2.4-5.0
Phosphorus (% TS)	0.8-2.8	0.5-0.7
Potash (K_2O, % TS)	0-1	0.5-0.7
Cellulose (% TS)	8-15	7.0-9.7
Iron (Fe, g/kg)	2-4	-
Silica (SiO_2, % TS)	15-20	-
pH	5.0-8.0	6.5-8.0
Grease and fats (%, TS)	7-35	5-12
Protein (%, TS)	20-30	32-41
Alkalinity (mg/L as $CaCO_3$)	500-1500	580-1100
Energy content (MJ/kg TS)	23-29	19-23

Anaerobic digestion is one of the best-implemented technologies for the treatment of sewage sludge, especially in large plants and usually operated under mesophilic range. During the stabilization of the sludge by AD, a part of the organic matter contained in the waste material is converted into methane usable as energy source thanks to its considerable HHV (35.8 MJ/m^3). On the other hand, and from a biorefinery point of view, the digestate obtained as a solid by-product can also be valorized; either as land application or as a biofuel. Digesters well-operated at mesophilic regime, with typical volumetric load (0.8-1.6 kg VS/m^3·d) can reach a VS digestion up to 55% and a biogas production in the range 0.75-1.12 m^3/kg $VS_{digested}$ [122,123].

1.4.2. New approaches for sewage sludge management by hydrothermal carbonization

HTC coupled with AD may be an effective and economical choice compared with conventional mesophilic anaerobic digestion of mixed sludge (Fig. 1.6 a), taking into account its high final disposal costs (80-100 € per ton in Europe) [40]. Currently, the implementation of HTC on sludge treatment line have been proposed (Fig. 1.6 b), in view of the amenability of the liquid fraction to be digested [65,68,69]: After AD, dewatered digestate is processed applying HTC. The HTC slurry is then dewatered, resulting a hydrochar with a dry matter content up to 70% reducing its volume between three and four times and with a HHV of 11.7 MJ/kg [39,75]. The liquid fraction can be recirculated to the anaerobic digester increasing soluble COD and, therefore, methane yield [76].

Another option to produce power from hidrochar, proposed by Heidari et al. [124], is combininig hydrothermal carbonization, anaerobic digestion, and gasification (Fig. 1.6 c). The hydrochar and the gas, mostly CO_2, released during the HTC process can be used to produce Syngas by gasification, and the process water could be valorized by anaerobic digestion using low carbonization temperatures (<210 ºC) to avoid the formation of recalcitrant compounds.

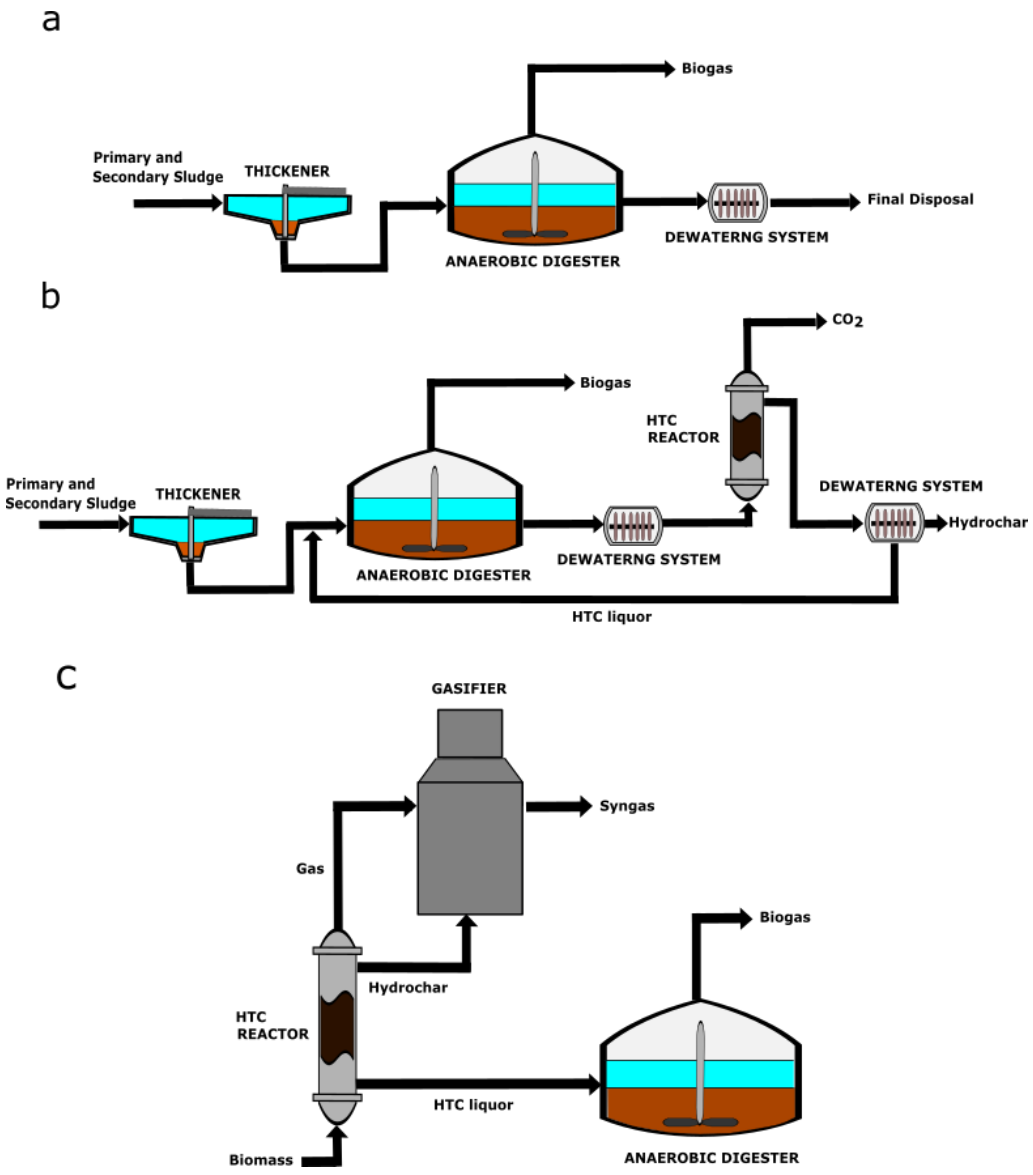


Fig. 1.6. Traditional sludge management (a), AD of sewage sludge+HTC of digestate coupling (b) (modified from Merzari et al. [40]), combination of HTC, AD, and gasification (c) (modified from Heidari et al [124]).

1.5. Objectives

HTC is a thermochemical process ables to convert low value wet biomass such as sewage sludge into hydrochar, a solid with intermediate characteristics between those of peat and coal, convertible in dry pellet, which can be used for energy exploitation, as soil improver or adsorbent, or converted to other added-value products [45,125–127].

Sewage sludge is the residue generated during the wastewater treatment processes. In general, its characteristics depend on the type of wastewater, the type of treatment and its operational strategies. Depending on the wastewater treatment stage in the wastewater handling units, sludge is categorized in primary sludge if produced during primary wastewater settlings (physical and/or chemical); secondary or waste activated sludge, if produced during secondary biological treatments; mixed sludge, which is a primary and secondary sludge mixtures, and tertiary sludge, if produced during tertiary or advanced wastewater treatments. The produced sludge can be further processed in the sludge treatment-line, where it can be stabilized by means of digestion processes (digested sludge) and dewatered by means of solid/liquid separation systems (dewatered sludge).

HTC of sewage sludge has been studied by several authors for different purposes. As for other kinds of feedstock, most studies focused on the solid phase, the hydrochar, to convert sludge to a valuable product, improving its dewaterability [52]. Many authors studied hydrochar, in order to exploit it for energy purposes as a renewable biofuel [7,27,42,44– 46], as well as a renewable biomass for biogas production [128]. Some authors focused on the use of hydrochar as adsorbent [49,50] and soil improver [7,51,125].

HTC process water from sewage sludge, which could contain up to 15% of the initial carbon present in the sewage sludge, mainly as acetic acid [69], is characterized by high TOC concentration (3.7–62 g/L), and COD concentration (12.7–64 g/L). In the case of digestate, COD and TOC concentration increased 7-fold and 10-fold after HTC treatment, respectively, as compared to the untreated digestate [76]. The high organic content of HTC process water allows for its valorization through the AD process, which has been investigated by several research groups [69,73,80,82,129]. Concerning agricultural residues, several biomasses were first treated by HTC producing HTC process water, that was fed to AD for energy valorization, such as orange pomace [65], brewer’s spent grain [82], corn silage [67], thin stillage [81], seaweed [75] and food waste [130].

The overall objective of this doctoral thesis was the evaluation of a new concept for sewage sludge management – dewatered waste activated sludge (DWAS) and thickened primary sewage sludge (PSS) – by a combination of hydrothermal carbonization (HTC) and anaerobic digestion. In this way, initially the best condition for hydrochar production from DWAS was studied, looking for a product with optimized HHV. Moreover, with the aim to produce low-cost adsorbents with a tunable porous structure, physical and chemical activation of the obtained hydrochar was performed to generate activated carbons. On the other hand, the liquid fraction from HTC (LF) obtained after DWAS carbonization was valorized by anaerobic digestion and co-digestion with PSS and the organic fraction of municipal solid waste (OFMSW).

The overall objective develops through the following specific objectives:

- To establish the optimal condition —temperature and reaction time — of HTC of DWAS for the production of a renewable solid fuel (hydrochar).
- To study the production of activated carbons from hydrochar (precursor) by physical and chemical activation.
- To study the potential valorization of the LF of DWAS by anaerobic digestion, evaluating the influence of the inoculum source, the inoculum concentration, and the inoculum to substrate ratio.
- To assess a new concept for sewage sludge management consisting on the mesophilic anaerobic co-digestion of mixtures of the LF of DWAS and PSS, in batch and semi-continuous modes, taking into account the inoculum source, the feed mixture ratio (PSS/LF), the temperature regime and the organic loading rate.
- To study the anaerobic co-digestion of the LF of DWAS and the OFMSW using different co-substrate ratios (LF/OFMSW) and temperature regimes, after optimizing the OFMSW substrate pretreatment (grinding and sieving).

This Ph.D. thesis has been carried out in the Laboratories of the Chemical Engineering Department at Autonomous University of Madrid and it is included in the Ph.D. Program in Applied Chemistry, which is regulated through the Spanish Law RD1393/2017.

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Chapter 2:

Materials and methods

2.1. Hydrothermal carbonization experiments

2.1.1. Dewatered waste activated sludge

DWAS (15%, wt.) used in each hydrothermal carbonization experiment carried out was collected from a full-scale membrane bioreactor (MBR) treating cosmetic wastewater (Madrid, Spain) and was stored at -20 ºC until used. A representative analysis of the raw material, dried in an oven at 55 ºC for 24 h, is showed in Table 2.2.1.

Table 2.1.1. Representative analysis of the dewatered waste activated sludge (composition in % wt., d.b.).

C (%)	41.5±0.1	**Na (mg/g)**	11.6±0.2
H (%)	6.0±0.1	**Mg (mg/g)**	0.7±0.1
N (%)	6.8±0.1	**Al (mg/g)**	15.7±0.2
S (%)	0.7±0.1	**P (mg/g)**	20.8±0.4
O[a] (%)	31.3±0.1	**K (mg/g)**	7.4±0.1
Ash content (%)	13.7±0.1	**Ca (mg/g)**	2.7±0.2
Volatile matter (%)	73.6±0.1	**Ti (mg/g)**	0.6±0.1
Fixed carbon (%)	12.7±0.1	**Fe (mg/g)**	0.2±0.1
pH	7.0±0.2	**Mn (mg/g)**	0.2±0.1

[a]Calculated by difference O=100–(C+H+N+S+Ash)

2.1.2. HTC reactor

The hydrothermal carbonization (HTC) of DWAS was performed on a ZipperClave® 316 stainless steel reactor electrically heated (Autoclave Engineers, United Stated of America) with a working volume of 4 L (127 mm of inside diameter and 312 mm of inside length) and a maximum allowable working pressure of 151 bar at 232 ºC. The pressure vessel was equipped with a Rushton impeller (diameter: 50.8 mm) and a bottom flush valve. The main seal of the reactor was an o-ring in viton material. The temperature and stirring rate were controlled using an Iberfluid controller (IB62). The autoclave was equipped with a serpentine cooler located inside the reactor.

2.1.3. Experimental design

The effect of process temperature (140-220 ºC) and reaction time (0.5-4 h) in the hydrothermal carbonization of DWAS was studied by a response surface methodology based on a central composite rotatable design. By using the Minitab® 17 software, 13 runs were generated (4 factorial point, 4 axial point and 5 replicates of the central point) with an alpha value of ±1.414.

For each experiment, 1.5 kg of DWAS was used. Once the reactor was closed, oxygen was swept away from the system by flushing with pure N_2 (99.99%) for 2 min. The working temperature was reached at a 3 ºC/min heating rate. The reaction was stopped with tap water using a serpentine cooler located inside the reactor. For all HTC experiments the reactor was cooled from the desired temperature reaction at a cooling rate lower than 4 ºC/min. The slurry obtained (470 g of wet hydrochar and 530 g of the liquid fraction (LF) for each kg of wet material treated) was centrifuged (1400 g for 1 h) by a SIGMA 3e16L centrifuge equipped with a fixed angle rotor (cod. 12159). The liquid fraction was recovered by filtration (0.45 mm) and was maintained at 4 ºC to be used as substrate of the anaerobic digestion tests performed. The solid fraction was washed several times with ethanol and deionised water, and dried at 55 ºC for 24 h. The resulting solid was ground and sieved to a particle size in the range of 0.1-0.25 mm.

2.1.4. Hydrochar activation

Air activation of hydrochars were performed in a horizontal tube furnace (Nabertherm RHTH 120/300/18/C42) at temperatures in the range 300-450 ºC for 2 h, using a heating rate of 10 ºC/min and an air flow rate of 30 NmL/min. The chemical activation was made by mixing the hydrochars with each activating agent (K_2CO_3, KOH, $FeCl_3$, and $ZnCl_2$) using a mass ratio of 1:1 at ambient temperature [1]. Mixed samples were heated in the tube furnace above described at 650 and 850 ºC for 1 h, using a heating rate of 10 ºC/min and a N_2 flow rate of 100 NmL/min. The activated carbons produced by chemical activation were washed with 1 M HCl aqueous solution, and then were rinsed with abundant deionised water up to neutral pH [1].

2.1.5. Materials characterization and analytical determinations

A summary of the main techniques employed for the characterization of the dewatered waste activated sludge, hydrochars, activated carbons, and the liquid fraction as well as the information that each one provided is collected in Table 2.1.2.

Elemental analysis: C, H, N, and S present in the sample were burned in excess of oxygen at temperature close to 1000 ºC and converted to combustion products such as CO_2, N_2 (gas), NOx, and SO_2. Then, C, H, S gases were measured in individual and selective infrared cells while N was analyzed by thermoconductivity. The elemental composition (C, N, S, and H) of each sample including sewage biosolid, hydrochars and activated carbons was determined by a CHNS analyzer (LECO CHNS-932).

Table 2.1.2. Analytical techniques.

Technique	Information	Equipment	Laboratory
Elemental analysis	Elemental composition (C, N, S and H)	LECO CHNS-932 analyzer	SIdI (UAM)
Proximate analysis	Moisture, volatile matter, ash, and fixed carbon	TA Instruments Q600 thermal analyzer	SIdI (UAM)
Higher heating value	Calorific value	IKA C2000 calorimetric bomb	CEBAS-CSIC
Total reflection X-Ray Fluorescence (TXRF)	Fe and Zn content in activated carbons	TXRF Extra-II Rich & Seifert spectrometer-Si–Li detector	SIdI (UAM)
Inductively coupled plasma atomic emission spectroscopy (ICP-MS)	Macro and micronutrients in the liquid fraction	Elan 6000 Sciex Perkin Elmer apparatus	SIdI (UAM)
N_2 adsorption-desorption isotherms	BET area and pore volume (meso- and microporosity)	Micromeritics Tristar 3020	Chem. Eng. (UAM)
Scanning electron microscope (SEM)	Morphology features of the hydrochars and activated carbons	Hitachi S-3000N Scanning electron microscope	SIdI (UAM)
Fourier transform infrared spectroscopy (FTIR)	Functional groups of the hydrochars and activated carbons	BRUKER IFS 66v/S Spectrometer	SIdI (UAM)
Gas chromatography/ion trap mass spectrometry	Identification of species in the liquid fraction	GC/MS; CP-3800/ Saturn 2200 system	SIdI (UAM)
Gas chromatography equipped with a thermal conductivity detector (TCD)	Biogas composition	ThermoFisher Trace 1300 230V	Chem. Eng. (UAM)
Gas chromatography equipped with a flame ionization detector (FID)	Individual volatile fatty acids	Varian 430 gas chromatograph	Chem. Eng. (UAM)

Moisture, ash, and volatile matter: the proximate analysis was done sequentially in a single procedure by thermogravimetric analysis (TGA) according to ASTM D7582 [2]. In this analysis, the mass sample loss is recorded as a function of time and temperature. For moisture determination, the sample is heated at 107±3 ºC for 1 h under N_2 atmosphere. For volatile matter analysis following the moisture determination, the temperature is raised from 107 to 900±15 ºC at a heating rate of 30 ºC/min and then held for 7 min. Finally, for ash analysis, the N_2 is switched to O_2. Then, the sample is kept at 900 ºC for 1 h. The fixed carbon is calculated by difference as follows:

$$Fixed\ carbon = 100\% - (moisture + volatile\ matter + ash) \quad \text{Eq. 2.1.1}$$

Higher heating values (HHV): the HHV is defined as the amount of heat released by the completed combustion of a sample with oxygen in a calorimeter (closed container) and include

the latent heat of vaporization of water. The HHV of dried solid samples (DWAS and hydrochars) were determined by a calorimetric bomb IKA C2000, according to the technical specification UNE-EN 5400 [3].

Metal content in liquid and solid samples: the metal content was obtained by inductively coupled plasma atomic emission spectroscopy (ICP-MS) using a model Elan 6000 Sciex Perkin Elmer apparatus.

The Fe and Zn content of activated carbons were analyzed by reflection X-ray fluorescence spectroscopy (TXRF), by Si–Li detector in a TXRF Extra-II Rich & Seifert spectrometer.

Surface chemistry of the activated materials: the surface chemistry was determined by X-ray photoelectron spectroscopy (XPS), using a 5700C model Physical Electronics apparatus, with energy dispersive X-ray spectroscopy analysis (EDAX) and Mg Kα radiation (1253.6 eV). The C1s peak position was set at 284.5 eV and used as reference for the assessment of the XPS peaks [4].

Textural properties: the porous structure of feedstock and carbonaceous materials was determined by N_2 adsorption–desorption at -196 ºC in a Micromeritics TriStar II 3020 apparatus. Samples were previously outgassed at 100 ºC and at a residual pressure of 10^{-3} Torr for 8 h. The surface area (S_{BET}) was determined applying the Brunauer-Emmett-Teller (BET) method. Micropore volume was estimated using the "t" method from the desorption data. The narrow mesopore (2-8 nm) was calculated from the nitrogen adsorbed in the p/p^0 range of 0.385-0.787. Moreover, surface area and micropore volume of the samples were also determined by CO_2 adsorption at 273 K. The surface area and the micropore volume were calculated using the Dubinin–Astakhov equation.

Morphology features of feedstock and carbonaceous materials: were analyzed by a Hitachi S-3000N scanning electron microscope (SEM) from samples fixed and sputter-coated with gold.

Fourier transform infrared spectroscopy (FTIR): FTIR was obtained by a Bruker IFS 66v/S spectrometer. Dry samples were mixed with KBr and pressed to prepare pellets that were scanned from 4000 to 400 cm^{-1} region with 250 scans per sample.

2.2. Anaerobic experiments

2.2.1. Liquid substrates

The liquid fraction (LF) recovered by filtration (0.45 mm) from the slurry after HTC of DWAS, was used as the main substrate on the anaerobic digestion tests performed. The main characteristics and composition of the LF are compiled in Table 2.1.3. Beside of LF, other two co-substrates were used in the different assays carried out: primary sewage sludge (PSS) and the organic fraction of municipal solid waste (OFMSW). The main characteristics and composition of PSS and OFMSW are included in Table 2.1.3 and Table 2.1.4, respectively.

Table 2.1.3. Main characteristics[a] and composition of LF from HTC and PSS used as AD substrates.

	Substrate	
	Liquid fraction	**Primary sewage sludge**
pH	4.9±0.2	5.1±0.1
TS (g/kg)	51.9±0.5	53.1±0.1
VS (g/kg)	24.0±0.5	45.7±0.1
TCOD (g O_2/L)	110.1±2.3	78.9±4.2
TKN (g N/L)	8.4±0.6	3.8±0.3
Na (mg/g)	1074.0±11.6[b]	3.1±0.1
Mg (mg/g)	23.2±1.3[b]	3.8±0.2
Al (mg/g)	15.8±0.7[b]	9.5±0.4
K (mg/g)	1182.7±66.1[b]	4.9±0.8
Ca (mg/g)	67.5±4.4[b]	33.0±0.3
Fe (mg/g)	32.5±0.1[b]	28.5±0.5

[a]Average values of three determinations with standard deviations.
[b](mg/L)

Table 2.1.4. Main characteristics of the organic fraction of municipal solid waste substrate.

	OFMSW (*ground+sieved*)
TS (g/kg)	466.5±3.0
VS (g/kg)	279.9±13.3
COD (mg O_2/g TS)	1163±7
C (%)	24.52±2.89
H (%)	1.64±0.46
N (%)	1.90±0.19
S (%)	0.13±0.05
Volatile fatty acids (mg COD/L)	2045±38

2.2.2. Inoculum source

In section 4.1, a granular anaerobic sludge from an industrial digester treating brewery wastewater under mesophilic conditions (35 ºC) was used. Its main characteristics were: pH: 7.6±0.1, TS: 61.9±0.9 g/L, VS: 55.7±0.9 g/L, TCOD: 91.2±1.4 g O_2/L and TKN: 2.2±0.1 g N/L.

In section 4.2, three different inocula, collected from industrial full-scale anaerobic reactors operating under mesophilic conditions (35 ºC), were used for the anaerobic digestion batch experiments:

- Inoculum 1 (BW): Granular inoculum obtained from an internal circulation anaerobic reactor treating brewery wastewater.
- Inoculum 2 (SB): Granular anaerobic sludge from an UASB reactor treating sugar beet effluents.
- Inoculum 3 (MS): Flocculent anaerobic sludge from a sewage sludge digester of a MWWTP.

The main characteristics of the three inocula are collected in Table 2.1.5 (average values of three determinations with standard deviations).

Table 2.1.5. Main characteristics of the inocula.

Inoculum source	pH	TS (g/kg)	VS (g/kg)	TCOD (g/L)	TKN (g N/L)
BW	7.6±0.1	61.9±0.9	55.7±0.9	91.2±1.4	2.2±0.1
SB	7.9±0.1	162.4±4.0	37.8±0.6	73.4±0.1	4.4±0.1
MS	7.2±0.1	43.3±0.3	26.5±0.3	43.5±1.2	2.2±0.1

In section 5.1, two different inocula were used: (i) An anaerobic flocculent sludge from a full-scale mesophilic digester treating mixed sewage sludge, and (ii) a granular inoculum obtained from a high rate anaerobic reactor, which treats brewery wastewater (Table 2.1.6.).

Table 2.1.6. Representative analysis[a] of flocculent and granular inocula.

	Inoculum	
	Flocculent sludge	**Granular sludge**
pH	6.9±0.1	7.2±0.2
TS (g/kg)	21.1±0.1	46.1±0.7
VS (g/kg)	13.9±0.3	40.3±0.1
TCOD (g O_2/L)	24.8±0.8	91.2±1.4
TKN (g N/L)	3.9±0.2	5.1±0.1

[a]Average values of three determinations with standard deviations.

In section 5.2, the mesophilic digesters used were seeded with inoculum from a WWTP full-scale mesophilic digester operating in Madrid (Spain). This mesophilic inoculum was adapted at 55 ºC for thermophilic experiments according to De la Rubia et al. [5]. Table 2.1.7 summarizes the characteristics of the inoculum.

Table 2.1.7. Representative characteristics of inocula.

	Inoculum	
	Mesophilic inoculum	**Thermophilic inoculum**
pH	7.5±0.1	8.1±0.1
Total solids (g/kg)	31.0±1.1	21.0±0.8
Volatile solids (g/kg)	20.5±0.1	12.5±0.1
TCOD (g O_2/L)	43.5±1.2	36.6±3.3
TKN (g N/L)	3.9±0.2	4.0±0.3

In section 6.1, the anaerobic inoculum used was the digestate from mesophilic anaerobic reactor that treats the OFMSW in a municipal solid waste treatment plant (MSWTP) located near Madrid, Spain. The main characteristics of this inoculum were: pH, 8.2±0.1; TS: 136.8±0.6 g/kg; VS: 70.7± 0.8 g/kg; and TCOD: 84.2±6.5 g/L.

In section 6.2, the mixed anaerobic culture used as thermophilic inoculum was obtained by directly switching the inoculum used on section 6.1 from mesophilic (35 ºC) to thermophilic conditions (55 ºC) according to De la Rubia et al. [5]. The main properties of that thermophilic inoculum were as follows: pH 8.2±0.1, total solids: 97.9±0.4 g TS/kg; volatile solids: 45.3±0.5 g VS/kg; and TCOD: 36.6±3.3 g O_2/L.

2.2.3. Experimental set up

Batch experiments was performed in 120 mL glass serum vials, filled with 60 mL of a suspension of inoculum, substrate and a basal medium with macro- and micronutrients (Table 2.1.8.) following the Holliger et al. [6] and Rincon et al. [7] recommendations. The reaction medium was previously flushed with N_2 (99.99%) for 3 min to achieve anaerobic conditions. Then, the vials were sealed with rubber stoppers and metallic crimps (Merck, Germany). The vials were maintained in a static incubator — manually mixed daily — or using a thermostatic water bath shaker at mesophilic (35±1 ºC) or thermophilic (55±1 ºC) temperature as appropriate.

Table 2.1.8. Nutrient and trace element solutions used in batch experiments [7].

Nutrient solution composition	**Concentration (g/L)**
NH_4Cl	1.4
K_2HPO_4	1.25
$MgSO_4 \cdot H_2O$	0.5
$CaCl_2 \cdot 2H_2O$	0.05
Yeast extract	0.5
Trace element solution	5.0*
Trace element solution composition	**Concentration (mg/L)**
$FeCl_3 \cdot 4H_2O$	2000
$CoCl_2 \cdot 6H_2O$	2000
$MnCl_2 \cdot 4H_2O$	500
$CuCl_2 \cdot 2H_2O$	38
$ZnCl_2$	50
H_3BO_3	50
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	50
$AlCl_3 \cdot 6H_2O$	90

*The amount of trace element solution added to the nutrient solution are expressed as mL of trace solution per L of nutrient solution (mL/L).

For each condition studied, nine fed reactors were run (Fig. 2.2.1.). The 9 reactors were initially fed and loaded with the required amounts of the substrate or co-substrates, six being sacrificed and removed each day initially, and then weekly until the end of the experiment, with the aim to check the evolution of singular parameters of anaerobic digestion: pH, partial and total alkalinity, volatile fatty acids, soluble COD, TOC, TKN, total ammonia nitrogen. The other three reactors were used for biogas analysis (volume and composition) only. Moreover, three blank runs (for subtracting the methane production due to biomass decay and the possible presence of residual substrate in the inoculum) and three positive controls (tests with starch as only substrate) were carried out. All experiments were allowed to develop until no significant biogas production was observed and biodegradation was thus essentially completed as in the controls with starch (≅350 mL CH_4/g COD_{added}).

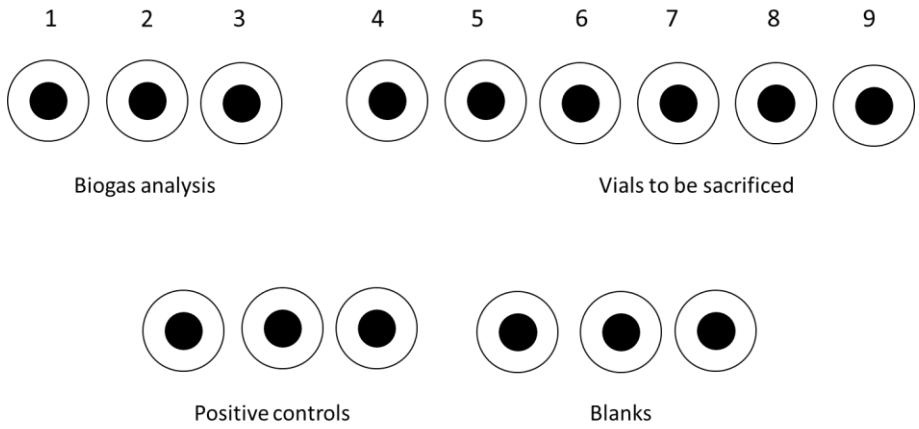

Fig. 2.2.1. Operational sequence used in each run.

Another *batch experiments* were performed in an Automatic Methane Potential Test System (AMPTS). This analytical device developed by Bioprocess Control AB (Lund, Sweden) was equipped with 15 test vials (500 mL) running in parallel. Thus, a digital pulse was generated when a gas volume of biogas (10 mL) flow through the system, registering only CH_4 flow since gases such as H_2S and CO_2 are absorbed and removed by a NaOH solution (3 M). Each bottle was mechanically mixed (100 rpm) with a time period of 1 min (ON/OFF switch). An integrated data acquisition system (AMPTS 3.0.3) was incorporated. Methane released from the digestion bottles was measured using a wet gas-flow measuring system with a multi-flow cell arrangement [8–10].

Semi-continuous experiments were carried out in borosilicate glass digesters. Each reactor has a total volume of 2.8 L and a working volume of 2 L. The temperature was adjusted by recirculating tap water through the double wall of the digester. Heat losses were minimized by using insulating coats which also reduced the amount of daylight reaching the reactors. Continuous stirring in the reactors was provided by direct drive stirrers furnished with holed paddles. The reactors were operated in a semi-continuous mode (one feed per day). Attainment of the steady-state under each set of conditions tested was verified after a period equivalent to 3 times HRT by checking the effluents for constancy in their properties. Samples for characterization were withdrawn during each steady-state period.

2.2.4. Analytical methods

pH: this measurement was performed by a pHmeter Crison 20 (Crison Instruments, Spain) according to standard method 4500H [11]. The pHmeter was calibrated with 4 and 9 standard

pH solution (Panreac). The sensibility of the instrument was ±1mV, corresponding to 0.01 pH units.

Alkalinity: partial and total alkalinity (PA and TA) was measured by pH titration to 5.75 and 4.3, following the recommendations by Jenkins et al. [12]. The titration process was carried out by a Titromatic 2S Titrator (Crison Instruments, Spain) with H_2SO_4 0.02 N (Panreac). It was calibrated with 4 and 9 standard pH solution (Panreac), before the measurements.

The partial and total alkalinity were calculated as follows:

$$Alk_{partial} = \frac{V_A \cdot N \cdot 50000}{V} \quad \text{Eq. 2.2.1}$$

$$Alk_{total} = \frac{V_B \cdot N \cdot 50000}{V} \quad \text{Eq. 2.2.2}$$

Where V_A is the volume of the H_2SO_4 necessary to reach pH 5.75, V is the volume of the sample (2 mL), N is the normality of H_2SO_4 (0.02 N), and V_B is the volume of the H_2SO_4 necessary to reach pH 4.3.

Soluble chemical oxygen demand (SCOD): chemical oxygen demand (COD) is defined as the amount of a specified oxidant, usually potassium dichromate that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. The dichromate ion ($Cr_2O_7^{2-}$) is reduced to the chromic ion (Cr^{3+}). Both organic and inorganic components of a sample are subject to oxidation, but in most cases the organic component predominates and is of the greater interest. This determination was carried out following the method 5220D [11]. An amount of sample (2.5 mL) was placed in a culture tube, and the reagents (1.5 mL of potassium dichromate, and 3.5 mL of sulfuric acid-silver sulfate (catalyzer)) were added carefully. After mixing, the mixture was digested in a thermoreactor Velp ECO-16 (Velp Scientifica, Italy) at 150 ºC for 2 h. Finally, the sample was cooled at room temperature, and COD concentration was determined measuring the absorption of each sample and blank sample at 420 nm or 600 nm in a UV-6000PC spectrophotometer (Jinan Precision Testing Equipment, China).

Total chemical oxygen demand (TCOD): the TCOD was determined following the method proposed by Raposo et al. [13], which was based on the DIN 38414-S9. 250 mg (solid or concentrate sample) or 1 mL (liquid sample) was digested with 20 mL $K_2Cr_2O_7$ 1.2 N, 30 mL

sulfuric acid with silver sulfate —10 g Ag_2SO_4/L H_2SO_4 (Panreac, 96% wt.) in glass digestion vessels (40 mm X 300 mm). The reagents and the sample were mixed and digested in a heating block ECO25 (Selecta, Spain) at 150 ºC for 2 h. Then, the sample was left to cool at ambient temperature. The COD concentration was measured by titration with ferrous ammonium sulfate (FAS) 0.5 N (Panreac) using ferroin solution as indicator (Panreac). The end point was reached when the color changes from light to dark green. As primary standard, a solution of potassium hydrogen phthalate (50 g/L) was used. The COD was calculated using the following equations:

$$COD\left(\frac{mg\ O_2}{g\ VS}\right) = \frac{(FAS_{blank} - FAS_{solid\ sample})\ \cdot\ N_{FAS} \cdot\ 8}{w_{solid\ sample}} \qquad \text{Eq. 2.2.3}$$

$$COD\left(\frac{mg\ O_2}{L}\right) = \frac{(FAS_{blank} - FAS_{liquid\ sample})\ \cdot\ N_{FAS} \cdot\ 8000}{V_{liquid\ sample}} \qquad \text{Eq. 2.2.4}$$

Where FAS_{blank} is the volume of FAS (0.5 N) used in the titration of the blank sample (mL), $FAS_{solid\ sample}$ is the volume of FAS used in the titration of the solid sample (mL), $FAS_{liquid\ sample}$ is the volume of FAS used in the titration of the liquid sample (mL). N_{FAS} is the concentration of reducing reagent (N), $w_{solid\ sample}$ is the weight of dry solid sample (g VS) while $V_{liquid\ sample}$ is the volume of liquid sample (mL).

Total Kjeldahl nitrogen (TKN): the TKN comprises organic and ammonia nitrogen. The determination of TKN was carried out into three steps:

i) Digestion: firstly, 1000 mg of sample (if solid) or 1 mL (if liquid) was acidified with 15 mL of concentrated H_2SO_4 85% wt. (Panreac). In addition, 5 g of catalyst [(Cu–Se) (1.5% $CuSO_4 \cdot 5H_2O$+2% Se)] (Panreac) were added. Then, the sample was digested sequentially in a Bloc Digest 12 thermoblock (Selecta, Spain) for 15 min at 150 ºC, 15 min at 250 ºC, and 90 min at 390 ºC.

ii) Distillation: before starting of distillation, 5 mL of sodium hydroxide (6 N) were added automatically to the digested sample and it was distilled for 5 min in a steam distillation system Pro-Nitro S (Selecta, Barcelona Spain). The distillate was collected into an Erlenmeyer flask which contains 25 mL of a boric acid indicator solution (20 g boric acid and 10 mL of mixed indicator (methyl red-bromocresol green (Panreac)) per liter).

iii) Titration: the distillate was titrated with sulfuric acid 0.02 N (Panreac). The end point was reached when the color changed from pink violet to emerald green. For blank (deionized water) less than 0.2 mL of 0.02 N sulfuric acid was needed. The TKN was calculated using Eq. 2.2.5.

$$\frac{mg\ NH_3 - N}{L} = \frac{\left(V_{sample} - V_{blank}\right)_{H_2SO_4} \cdot 14000}{V_{sample}} \quad \text{Eq. 2.2.5}$$

where V_{sample} is the volume of sample used and V_{blank} is the volume of deionized water (blank).

Total organic carbon (TOC): the method to determine TOC is based on the complete catalytic oxidation combustion at high temperature (ca. 720 ºC), to convert organic carbon to CO_2. The gas generated was analyzed with a non-dispersive infra-red (NDIR) sensor. The total organic carbon was obtained by the difference between total carbon (TC) and total inorganic carbon (TIC). After filtering the sample (glass microfiber filter, 0.45 µm), the measurement was carried out with an automatic analyzer TOC-VCPN (Shimadzu). Calibration curves using potassium hydrogen phthalate (1000 mg C/L) and sodium hydrogen carbonate (1000 mg C/L) as total carbon and inorganic carbon standard solutions were prepared, respectively. Each sample was analyzed for triplicate.

Total suspended solids: this determination was performed following the Standard 2540D [11]. A well-mixed sample was filtered through a weighed standard glass-fiber filter and the residue retained on the filter was dried to a constant weight at 103 to 105 ºC. The increase in weight of the filter represents the total suspended solids. The concentration of total suspended solids was calculated as follows:

$$Total\ suspended\ solids = \frac{w_d - w_f}{V_f} \quad \text{Eq. 2.2.6}$$

where w_d is the weight of the sample dried, w_f is the weight of the filter, and V_f is the sample volume that was filtered.

Volatile suspended solids: the dried filter used for TSS determination was ignited in a muffle furnace at 550 ºC for a minimum of 30 min to remove volatile solids. The remaining solids represent the fixed total suspended solids while the weight lost on ignition was the volatile solids. At least triplicate analysis was performed for each sample.

$$Volatile\ suspended\ solids = \frac{w_d - w_c}{V_f} \quad \text{Eq. 2.2.7}$$

where w_d is the weight of filter and the sample dried, w_c is the weight of filter and residue after ignition, and V_f is the sample volume that was filtered.

Conductivity: the conductivity of the process water of HTC was measured with a conductimeter GLP 31 (Crison Instruments, Spain). This device was calibrated with conductivity standard (Panreac) of 147 and 1413 µS/cm, respectively.

Volatile fatty acids: individual VFA concentrations (from acetic to heptanoic, including iso-forms) were determined by gas chromatography (GC) (Varian 430-GC) equipped with a flame ionization detector (FID) and a capillary column filled with Nukol (polyethylene glycol modified by nitroterephthalic acid). Sample preparation was carried following the de la Rubia et al. [14] recommendations: before starting the injection, a volume sample of 900 µL was mixed with 150 µL of H_3PO_4 (1:2 v:v) to adjust pH below 2.0 and 150 µL volume solution of crotonic acid (Panreac) with a concentration of 2000 mg/L as an internal standard. This mixture was centrifuged to remove any solids and transferred to a 1500 µL GC vial. The sample injection volume was 1 mL. The temperatures of the injector and detector were maintained at 200 and 250 ºC, respectively, while the column temperature was increased from 120 to 160 ºC with an increasing rate of 10 ºC/ min

Chemical species in the liquid fraction: the identification of species was performed by gas chromatography/ion trap mass spectrometry (GC–MS; CP-3800/ Saturn 2200) with an autosampler injector (Varian CP-8200), and a solid phase microextractor, (Carbowax/Divinylbenzene Yellow-Green). A Factor Four VF-5 ms capillary column (30 m long, 0.25 mm diameter) was used. Sample injection was carried out with split-less at 220 ºC, using He as carrier gas. The temperature program used in the GC/MS analyses ramped as follows: 40 ºC for 15 min and 15 ºC/ min until 250 ºC. The compounds were identified using the NIST 2008 Library.

Biogas volume and composition in batch experiments: the biogas was measured along the incubation period by manometric method except the experiments performed with AMPTS, described in the section 2.2.3, which were measured by volumetric method. The pressure was measured connecting the head space of the vial to an electronic pressure monitor (ifm, PN 7097).

The number of mole of gas (n_{gas}) was calculated from measured pressure using the gas laws:

$$n_{gas} = \frac{P_{gas} \cdot V_{headspace}}{RT_{gas}} \quad \text{Eq. 2.2.8}$$

Where n_{gas} is the number of moles of gas in the volume of headspace vial, P_{gas} is the mean of the registered pressure, $V_{headspace}$ is the volume of headspace in the vial, R is molar gas constant, and T is the incubation temperature (K). Equation 2.2.9 was used to adjust a gas volume to standard temperature and pressure (273 K, 1 atm).

$$V_{STP} = n_{gas}\left(\frac{R \cdot T_{STP}}{P_{STP}}\right) \quad \text{Eq. 2.2.9}$$

Where V_{STP} is the volume adjusted to standard pressure and temperature (273 K, 1 atm) using the International Union of Pure and Applied Chemistry (IUPAC) definition [15], n_{gas} is the number of mole of gas at incubation conditions, P_{STP} is the standard pressure (1 atm), and T_{STP} is the standard temperature (273 K). After registering the pressure, biogas was subsequently exhausted to re-establish atmospheric pressure.

For semi-continuous experiments biogas volumes were directly measured with a Ritter MilliGas counter (MGC-1 V3.4 PMMA) from Ritter Apparatebau GmbH and collected in Tedlar® gas sampling bags.

Biogas composition was determined by gas chromatography separation using a ThermoFisher Trace 1300 230V equipped with an 8 ft. x 1/8 in SS column packed with HayeSep Q 80/100 mesh and a thermal conductivity detector (TCD). The injection volume from batch or semi-continuous experiments was 1 mL. The temperatures of the injector and detector were maintained at 110 and 150 ºC, respectively. Helium was used as the carrier gas at a flow rate of 30 mL/ min. A standard gas (Praxair, S.A; composition: 7.35% H_2; 3.01% H_2S; 59.84% CH_4, and 29.8% CO_2) was used for system calibration. The analysis of standard gas was performed in triplicated at the beginning of the procedure. The volume of methane was calculated with Eq. 2.2.10.

$$V_{CH_4,STP} = x_{CH_4} \cdot V_{CH_4,STP} \quad \text{Eq. 2.2.10}$$

Where x_{CH_4} is the methane concentration.

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Chapter 3:

Production of inexpensive waste activated sludge-based adsorbents by hydrothermal carbonization and activation processes

J.A. Villamil, E. Diaz, M.A. de la Rubia, J.J. Rodriguez, A.F. Mohedano, Production of inexpensive waste activated sludge-based adsorbents by hydrothermal carbonization and activation processes. Submitted for publication

Abstract

Hydrothermal carbonization of dewatered waste activated sludge for production of hydrochar, which can be used as renewable solid fuel or as precursor of activated carbons has been studied. A central composite rotatable design was applied to analyze the effect of temperature (140-220 ºC) and reaction time (0.5-4 h) on the physical and chemical characteristics of hydrochars. Hydrochars were characterized by BET areas around 25 m^2/g, with a significant mesoporous contribution. The higher heating values of hydrochars varied from 19.5 to 22.3 MJ/kg. Carbon materials obtained by air activation (300-450 ºC) developed BET areas until 100 m^2/g for the lowest temperatures. Chemical activation with K_2CO_3, KOH, $FeCl_3$, and $ZnCl_2$ (650 and 850 ºC) provided BET areas in the range from 410 to 1030 m^2/g with an important contribution of meso (0.079-0.271 cm^3/g) and microporosity (0.136-0.398 m^3/g). The results obtained support the potential application of hydrothermal carbonization of dewatered waste activated sludge for the production of precursor of inexpensive activated carbons with tunable porous structure.

3.1. Introduction

Nowadays, the huge generation of sewage sludge in wastewater treatment plants claims new solutions for the management of this waste. In Spain, around 1,400,000 t (d.b.) of sewage sludge are annually generated, which are mainly applied in agriculture uses (70%) or landfilling (14%) [1]. In the last two decades, several methods of thermal valorization of sewage sludge, such as combustion [2], gasification [3–5], pyrolysis and/or activation [6–10] have been investigated.

These aforementioned technologies have high energy requirements for drying the raw material, need strict control of the pollutants emitted and, in many cases, suffer from the social and political opposition [11–13]. The hydrothermal carbonization (HTC), also referred to as wet torrefaction, is an exothermic process that allows the biomass transformation under mild temperatures (150-250 ºC) and low residence times (5-240 min) under autogenous pressure using water as reaction medium. Then, predrying step is not needed, which reduces energy consumption, and consequently, the operating cost is significantly lower.

HTC has been applied to a great variety of feedstocks: lignocellulosic biomass, with variable composition in hemicellulose (20-40%), cellulose (40-60%) and lignin (10-25%); and to non-lignocellulosic one, such as animal manure, sewage sludge food and municipal solid wastes, among others, which have significantly different composition [14–17]. As reaction

products, a gas phase is generated, mainly CO_2 (>90%) and small amounts of CH_4, H_2, and CO [18,19] and two by-products, a process water and solid phase (hydrochar) with a high carbon content [13]. The HTC process water, also referred as HTC liquor or HTC liquid fraction, could contain up to 15% of the initial carbon present in the sewage sludge and includes high concentration of organic compounds such as volatile fatty acids (formic, acetic and propionic acid), carbohydrates, aldehydes, furans, phenols, pyrazines, pyrroles, among others [20–22]. This HTC liquid fraction can be valorized by anaerobic digestion for methane production [21–27] or be used as fertilizer, since macro (nitrogen and phosphorous) and micronutrents (i.e., Al, Ca, Fe, Mg) are present [28]. Some researchers stated that the treatment of this process water could be also carried out by an aerobic treatment or wet air oxidation as well [29–31]. Hydrochar is formed by hydrolysis, decarbonylation, decarboxylation, dehydration, polymerization, and condensation reactions [29,32–34]. This could be directly used as a solid fuel with similar characteristic to bituminous coal [20,35] or apply as soil remediation and CO_2 sequestration, catalysis and absorption [16,36,37].

The production of low-cost catalyst supports and adsorbents from dewatered waste activated sludge (DWAS) have been previously studied by means of pyrolysis followed by physical or chemical activation to obtain activated carbons with relatively high surface areas and great quality of the textural properties [7,38]. Thus, this work aims to the valorization of dewatered waste activated sludge by hydrothermal carbonization to produce a hydrochar useful as solid fuel or as precursor of activated carbons. The effect of reaction time and process temperature along the HTC process was studied by applying a central composite rotatable design. Hydrochars were subjected to physical activation with air at different temperatures (300-450 ºC) and chemical activation with K_2CO_3, KOH, $FeCl_3$, and $ZnCl_2$ (650 and 850 ºC) in order to prepare activated carbons.

3.2. Materials and methods

3.2.1. Dewatered waste activated sludge

DWAS was collected from a full-scale MBR treating cosmetic wastewater (Madrid, Spain) and was stored at -20 ºC until be used. A representative analysis of the raw material, dried in an oven at 55 ºC for 24 h, is showed in Table 3.1.

Table 3.1. Representative analysis of the dewatered waste activated sludge (composition in % wt., d.b.).

C (%)	41.5±0.1	**Na (mg/g)**	11.6±0.2
H (%)	6.0±0.1	**Mg (mg/g)**	0.7±0.1
N (%)	6.8±0.1	**Al (mg/g)**	15.7±0.2
S (%)	0.7±0.1	**P (mg/g)**	20.8±0.4
O[a] (%)	31.3±0.1	**K (mg/g)**	7.4±0.1
Ash content (%)	13.7±0.1	**Ca (mg/g)**	2.7±0.2
Volatile matter (%)	73.6±0.1	**Ti (mg/g)**	0.6±0.1
Fixed carbon (%)	12.7±0.1	**Fe (mg/g)**	0.2±0.1

[a]By difference

3.2.2. HTC system set-up and hydrochar activation

HTC was performed in a ZipperClave® pressure vessel (4 L) electrically heated. For each experiment, 1.5 kg of DWAS (15% wt.) was used. The effect of process temperature (140-220 ºC) and reaction time (0.5-4 h) in the hydrothermal carbonization of DWAS was studied by a response surface methodology based on a central composite rotatable design. By using the Minitab® 17 software, 13 runs were generated (4 factorial point, 4 axial point and 5 replicates of the central point) with an alpha value of ±1.414. Once the reactor was closed, oxygen was swept away from the system by flushing with pure N_2 (99.99%) for 2 min. The working temperature was reached at a 3 ºC/min heating rate. The reaction was stopped with tap water using a serpentine cooler located inside the reactor. For all HTC experiments, the reactor was cooled from the desired temperature reaction at a cooling rate lower than 4 ºC/min. The solid fraction was recovered by centrifugation at 3500 rpm for 1 h, washed several times with ethanol and desionised water, and dried at 55 ºC for 24 h. The resulting solid was ground and sieved to a particle size in the range of 0.1-0.25 mm. The solid yield was determined according to the following (Eq. 3.1):

$$Solid\ yield\ = \frac{mass\ of\ dried\ hydrochar}{mass\ of\ dried\ waste\ activated\ sludge} \cdot 100 \qquad \text{Eq. 3.1}$$

The energy yield of the hydrochars was discussed in terms of energy density and energy recovery efficient obtained from Eq. 3.2 and 3.3 [39]:

$$Energy\ density = \frac{higher\ heating\ value\ of\ hydrochar}{higher\ heating\ value\ of\ DWAS} \qquad \text{Eq. 3.2}$$

$$Energy\ recovery\ efficiency\ (\%) = Hydrochar\ yield \cdot Energy\ density \quad \text{Eq. 3.3}$$

Carbon recovery in hydrochar ($H_{C,rec}$) was calculated as follows:

$$H_{C,rec} = \frac{C_{hydrochar} \cdot hydrochar\ mass}{C_{DWAS} \cdot mass\ of\ dry\ DWAS} \quad \text{Eq. 3.4}$$

Air activation of hydrochars were performed in a horizontal tube furnace (Nabertherm RHTH 120/300/18/C42) at temperatures in the range 300-450 ºC for 2 h, using a heating rate of 10 ºC/min and an air flow rate of 30 NmL/min [40]. The chemical activation was made by mixed the hydrochars with each activating agent (K_2CO_3, KOH, $FeCl_3$, and $ZnCl_2$) using a mass ratio of 1:1 at ambient temperature [40]. Mixed samples were heated in the tube furnace above described at 650 and 850 ºC for 1 h, using a heating rate of 10 ºC/min and a N_2 flow rate of 100 NmL/min. The carbon materials produced by chemical activation were washed with 1 M HCl aqueous solution, and then rinsed with abundant distilled water up to neutral pH [40].

3.2.3. Materials characterization and analytical determinations

The elemental composition (C, N, S, and H) of each material was determined by a CHNS analyzer (LECO CHNS-932). ASTM methods D3173-11, D3174-11, and D3175-11 were used to determine the moisture, ash, and volatile matter content, respectively. A calorimetric bomb (IKA C2000) was used for the determination of the higher heating values, according to the technical specification UNE-EN 5400. Each analysis was performed by triplicate being the standard deviation less than 5% in all cases. The porous structure of hydrochars and activated carbons was carried out by N_2 adsorption–desorption at -196 ºC in a Micromeritics TriStar II 3020 apparatus. Samples were previously outgassed at 100 ºC and a residual pressure of 10^{-3} Torr for 8 h. The surface area (S_{BET}) was determined applying the BET equation [41]. Moreover, surface area and micropore volume of the samples were also determined by CO_2 adsorption at 273 K. The surface area and the micropore volume were calculated using the Dubinin–Astakhov equation. SEM images were obtained using a Hitachi S-3000N apparatus from samples fixed and sputter-coated with gold. Fourier transform infrared spectroscopy (FTIR) was obtained by a Bruker IFS 66v/S Spectrometer. Dry samples were mixed with KBr and pressed to prepare pellets that were scanned from 4000 to 400 cm^{-1} region with 250 scans per sample. The metal content was obtained by inductively coupled plasma atomic emission spectroscopy (ICP-MS) using a model Elan 6000 Sciex Perkin Elmer apparatus. The total or bulk Fe and Zn loading total were analyzed by reflection X-ray fluorescence spectroscopy

(TXRF), while the surface chemistry of the activated materials were determined by X-ray photoelectron spectroscopy (XPS), as described elsewhere [42].

Process water obtained in the carbonization runs was also characterized. Liquid samples were previously filtrated with Whatman filter paper (1.2 mm). Analyzes of soluble chemical oxygen demand (SCOD) was performed according to the APHA Standard Methods [43]. Total organic carbon was measured with an automatic analyzers TOC-VCPN (Shimadzu), respectively. The species in the liquid fraction was identified by a CP-3800/Saturn 2200 Varian gas chromatograph with an autosampler injector (CP-8200, Varian) [22]. The analysis were performed in triplicates and the standard deviation was less than 5% in all cases. The database library NIST was used for the identifications of species. Individual volatile fatty acid (VFA) concentrations in the HTC liquor were determined by gas chromatography (Varian 430-GC) equipped with a flame ionization detector (FID) following the procedure described elsewhere [44].

3.3. Results and discussion

3.3.1. Chemical and structural characteristics of the hydrochars

Table 3.2 collects information on the energy properties of DWAS and carbon materials. The higher heating values (HHVs) were within the range of 19-22 MJ/kg showing an increase trend as reaction temperature increases. The hydrochar carbonized to the highest temperature (220 ºC-2.3 h) enhanced 1.27-fold the HHV with regard to the feedstock (17.6±0.1 MJ/kg). The HHV of this hydrochar was slightly higher than those of lignite and brown coal (<17.4 MJ/kg) and were within the range of sub-bituminous coal (17-24 MJ/kg). The increasing of the reaction severity, favors the carbon contents in the carbon materials as well as the energy density because of decarboxylation and dehydration reactions [20]. An opposite trend was observed for the energy recovery efficiency which varied from 40 to 67%.

Table 3.3 reports the physicochemical properties of solid fraction obtained at different temperatures of carbonization and operating reaction times. High solid yields achieved at temperatures lower than 180 ºC together with the values of carbon content of these samples are associated with a low carbonization degree of these raw materials. Hydrochar reactivity (solid yield) and volatile matter (VM) decreased as temperature within 180 and 220 ºC and reaction time increased, with values in the range of 35-49% and 63-76% (w/w), respectively. An increase of the ash contents with the carbonization temperature, in the range between 15-23%, was observed. This trend in ash content was due to the loss of VM along the HTC carbonization [45,46]. The ash values were fairly lower than the reported by Danso-Boateng et al. [20]

(23-39%) and Kim et. al [45] (33%) for hydrochars obtained from sewage sludge and digested sewage sludge, respectively; in both cases related to the higher ash content of the feedstock in comparison with the DWAS (13.7%) used in this study. The reactivity of hydrochars has been tried to be correlated with process temperature and reaction time using a second-order model [47]. The Levenberg-Marquardt algorithm was applied to fit the model to the experimental data using Minitab® 17 software. Solid yield could be fitted to the quadratic equation as follows: solid yield (%, wt.)=306.3-2.439T-14.47t+0.005838T^2+3.017t^2, where T was the temperature (ºC) and t the reaction time (h). The temperature was the most significant variable ($p \leq 0.001$) at the 95% confidence, while the reaction time was statistically no significant ($p \geq 0.05$). The results showed that the quadratic model was statistically significant since the calculated F-value (F_{cal}=80.91) was greater than the tabulated one (F_{tab}=9.12).

Table 3.2. Energy properties of carbon materials.

Sample	HHV (MJ/kg)	Energy density	Energy recovery Efficiency (%)
140 ºC-2.3 h	19.3±0.1	1.10	65.5
152 ºC-1 h	19.1±0.1	1.09	66.7
152 ºC-3.5 h	19.9±0.1	1.13	66.1
180 ºC-0.5 h	19.5±0.1	1.11	53.7
180 ºC-2.3 h	20.8±0.2	1.18	57.9
180 ºC-4 h	21.6±0.1	1.23	56.7
208 ºC-1 h	21.6±0.1	1.23	49.5
208 ºC-3.5 h	21.4±0.5	1.22	45.8
220 ºC-2.3 h	22.3±0.1	1.27	40.0

The elemental composition of hydrochars was arranged in a van Krevelen's diagram (Fig. 3.1). The H/C and O/C atomic ratios decreased as the reaction temperature increased from 150 to 220 ºC. The reduction in H/C and O/C atomic ratios of DWAS confirmed the significant role of dehydration and decarboxylation reactions along HTC process, as well as hydrolysis [29]. The H/C and O/C atomic ratios were 1.74 and 0.57 for the DWAS, far away from the obtained for bituminous coal and anthracite. As it is abovementioned, runs performed at temperatures lower than 180 ºC did not show significant carbonization. The most carbonized hydrochar (208 ºC-3.5 h) reached a reduction in the H/C and O/C atomic ratios of 14 and 24% with respect to DWAS. The fixed carbon (FC) were within the range of 8-16%, showing an increase trend as reaction temperature increases. Specifically, these hydrochars meet the quality standard of graded thermally treated and densified biomass fuels (ISO 17225-8) [48] in relation to HHV values (>17 MJ/kg) and sulphur content (<0.5%). However, they show volatile matter content lower than 75% and exceed the maximum nitrogen content (<3%) required to reduce NO_x

emissions. As alternatives to overcome this inconvenient, hydrochar from DWAS could be blended with coal or biomass residues [49], reducing the possible harmful emissions.

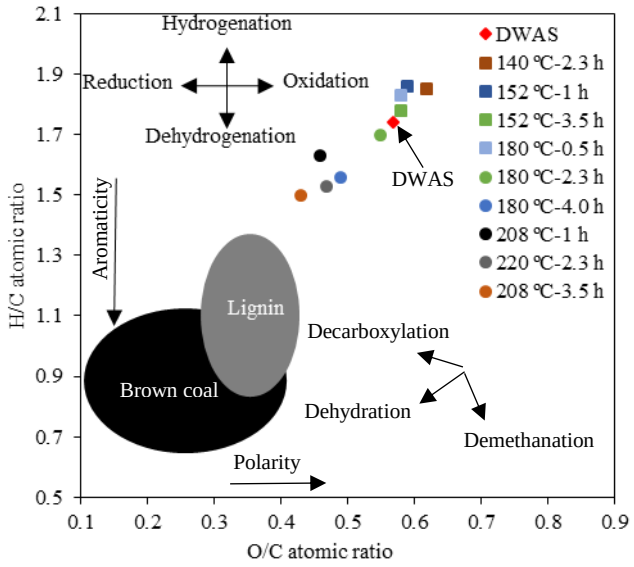

Fig. 3.1. Van Krevelen diagram of the DWAS and carbon materials obtained at different temperatures and reaction times.

Hydrochars showed a low-porosity development (S_{BET}<24 m^2/g) in line with previous works [49–52]. The low BET area values could be related to the partial blocking of meso- and mainly micropores by the presence in the hydrochar surface of volatile matter that has not been transferred to the process water during the HTC process [53]. Thus, mesoporosity presented a relatively significant contribution, with volume values up to 0.03 cm^3/g, similar to the hydrochars obtained from hydrothermally treated municipal sludge [50] and anaerobically digested maize silage [54]. To gain further insight into the microporosity for the hydrochars, CO_2 adsorption isotherms at 273 K was performed for hydrochar obtained at 208 ºC for 1 h. This provided a surface area of 252 m^2/g with a micropore volume of 0.154 cm^3/g while a pore width of 2.44 nm was found. Titirici [55] reported lower surface areas for glucose (183 m^2/g) and sucrose (173 m^2/g) hydrothermally treated at 180 ºC and the presence of ultramicropores (≅ 0.5 µm) as well.

Fig. 3.2 shows the effect of process temperature on the main nutrients and micronutrients in the carbon materials obtained. A decrease of N, K and Na content occurred as the temperature increased, which causes an enrichment of the liquid fraction in these components. P was retained in the materials obtained at low temperatures, while temperatures higher than 152 ºC were needed to transfer this element to the process water.

Table 3.3. Representative analysis of hydrochars (composition in % wt., d.b.).

Experimental conditions	Solid yield (%)	Fixed carbon (%)	Ash content (%)	Volatile matter (%)	Elemental composition (%)					$H_{C,rec}$ (%)	S_{BET} (m^2/g)	$V_{mesopores}$ (cm^3/g)
					C	H	S	N	O[a]			
140 ºC-2.3 h	59.7	12.0±0.1	15.8±0.1	72.5±0.3	39.6±0.3	6.1±0.1	0.3±0.1	5.6±0.1	32.9±0.2	57.0	-	0.001
152 ºC-1 h	61.5	11.5±0.1	15.0±0.1	73.5±0.1	40.6±0.1	6.3±0.1	0.4±0.1	5.9±0.1	31.7±0.1	60.2	-	0.001
152 ºC-3.5 h	58.5	11.1±0.1	17.1±0.1	71.8±3.3	40.4±0.9	6.0±0.1	0.2±0.1	5.2±0.1	31.3±0.1	56.9	5	0.006
180 ºC-0.5 h	48.5	8.1±0.1	16.4±0.1	75.4±1.7	40.5±0.1	6.2±0.1	0.3±0.1	5.6±0.1	31.1±0.2	47.3	-	0.001
180 ºC-2.3 h[b]	49.0	13.6±0.4	19.3±0.5	67.2±0.5	40.7±0.8	5.8±0.1	0.2±0.1	4.6±0.1	29.5±0.2	48.1	15	0.020
180 ºC-4 h	46.2	15.5±0.2	18.7±0.1	65.8±0.1	42.7±0.0	5.6±01	0.2±0.1	5.0±0.1	27.7±0.2	47.5	20	0.027
208 ºC-1 h	40.3	14.9±0.1	19.7±0.1	65.4±0.3	43.1±0.2	5.8±0.1	0.2±0.1	4.6±0.1	26.5±0.3	41.9	21	0.026
208 ºC-3.5 h	37.7	15.4±0.1	21.3±0.1	63.2±0.1	43.6±0.1	5.5±0.1	0.3±0.1	4.5±0.1	24.9±0.1	39.6	23	0.032
220 ºC-2.3 h	31.6	15.8±0.2	22.8±0.1	63.3±1.6	41.5±0.1	5.3±0.1	0.2±0.1	4.1±0.1	26.1±0.2	31.6	24	0.031

[a]By difference.
[b]Central point

There are no quality standards for the application of hydrochar as soil amelioration [56]. However, the biochar obtained by pyrolysis must fulfil the European Biochar Certificate, which could be used as reference for hydrochar [57]. In this sense, the hydrochars do not fulfil some of the soil-ameliorating properties, such as carbon content (>50%), molar H/C atomic ratio (<0.7) and the molar O/C atomic ratio (<0.4). From soil amendment point of view, macronutrients such as NPK are beneficial for plant growth. NPK weight percentages values of 6.8/6.0/1.0 and 6.8/2.5/1.0 were obtained for the materials carbonized at 152 and 208 ºC for 1 h, respectively. NPK ratios lower than commercial fertilizer (15/15/15) were observed [58]. Thus, the use of hydrochar to improve soil quality as supplemental fertilizer can be a feasible option, reducing the costs associated with a classical fertilizer application. Finally, mention should be made that several works reflect the negative effect of hydrochar as soil additive since plants growth could be affected [59–62].

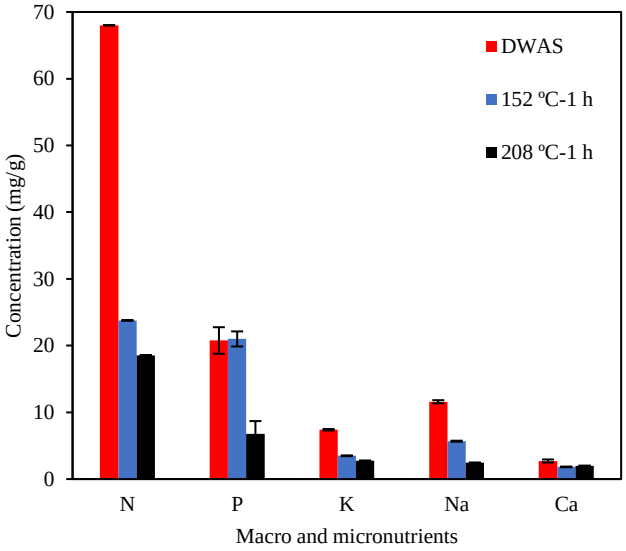

Fig. 3.2. Main nutrients and micronutrients in carbon materials obtained at 152 and 208 ºC for 1 h.

Table 3.4 shows the main characteristics of the process water resulting of the carbonization experiments. SCOD and TOC values were in the range of 81-96 g O_2/L and 36-48 g C/L, respectively, significant higher than those reported for sewage sludge [20] and sewage digestate [28], due to the low initial solid concentration (<4.5% wt.) used in these experiments. The process water obtained at 208 ºC for 1 h was analyzed and also contained high concentrations of acetic (3532±123 mg/L), propionic (620±10 mg/L) and iso-valeric acids (78±19 mg/L), which prevents its application as liquid fertilizer in agriculture. Total volatile fatty acid concentration higher than 3000 mg/L could be toxic for seed germination and plant growth

[63,64]. Also the NPK content found in the process water (≅18/1/2) is far away to the recommended for the effective growing of plants (5/10/10), and the high N:P ratio is considered a growth-limiting factor [65]. In order to valorize the HTC liquor, anaerobic digestion has been used as feasible option, which could permit energy recovery due to its high organic matter content. Several studies have also digested the process water from HTC of a number of wastes such as microalgae [26], digestate [28], spend coffee [66], sewage sludge [21,22], orange peel [13], and thin stillage [67] with good results. Thus, hydrothermal carbonization coupled with anaerobic digestion could be interesting and versatile technique to produce energy from DWAS in form of hydrochar and methane.

Finally, process water showed an acid pH, except for the runs performed to the most severe HTC conditions (208 ºC for 3.5 h and 220 ºC for 2.3 h), probably due to the balance between organic acids production [44] from the decomposition of monosaccharides [68], and CO_2 and ammonia produced by decarboxylation and deamination reactions [69,70]. The conductivity of process water increased at higher HTC severity, ranging from 11 to 21 mS/cm. Escala et al. [71] found similar values (11-14 mS/cm) in the process water resulting from HTC of sewage sludge. This parameter has gained special attention for checking the progress of the HTC process. Gallifuoco et al. [72] proposed to use the conductivity of the HTC liquour as a measure of the carbonization grade. They reported that the conductivity was correlated with the carbon content.

Fig. 3.3 shows the GC/MS analysis of the process water obtained at 208 ºC for 1 h and the compounds identified were collected in Table 3.5. Process water revealed a fairly complex composition with the presence of ketones, phenolic compounds, and Maillard reaction products such as heterocyclic nitrogen compounds (pyrazines and pyrazoles) from proteins, being some of them previously reported after HTC of sewage sludge [20,22–24,68].

Table 3.4. Representative analysis of the process water from HTC experiments.

Sample	pH	Conductivity (mS/cm)	SCOD (g O_2/L)	TOC (g C/L)
140 ºC-2.3 h	5.0	11.4	80.9±0.8	35.9±1.1
152 ºC-1 h	5.0	10.7	80.5±1.7	44.4±0.8
152 ºC-3.5 h	5.2	14.1	95.5±0.4	45.5±0.9
180 ºC-0.5 h	4.8	11.1	87.4±0.7	40.0±0.9
180 ºC-2.3 h	5.0	16.7	87.8±1.5	45.2±1.0
180 ºC-4 h	5.0	18.8	95.4±0.1	48.4±1.0
208 ºC-1 h	5.1	17.0	84.7±1.1	42.6±1.0
208 ºC-3.5 h	6.4	21.2	87.3±1.2	44.0±1.0
220 ºC-2.3 h	7.4	20.1	81.5±1.9	40.1±0.9

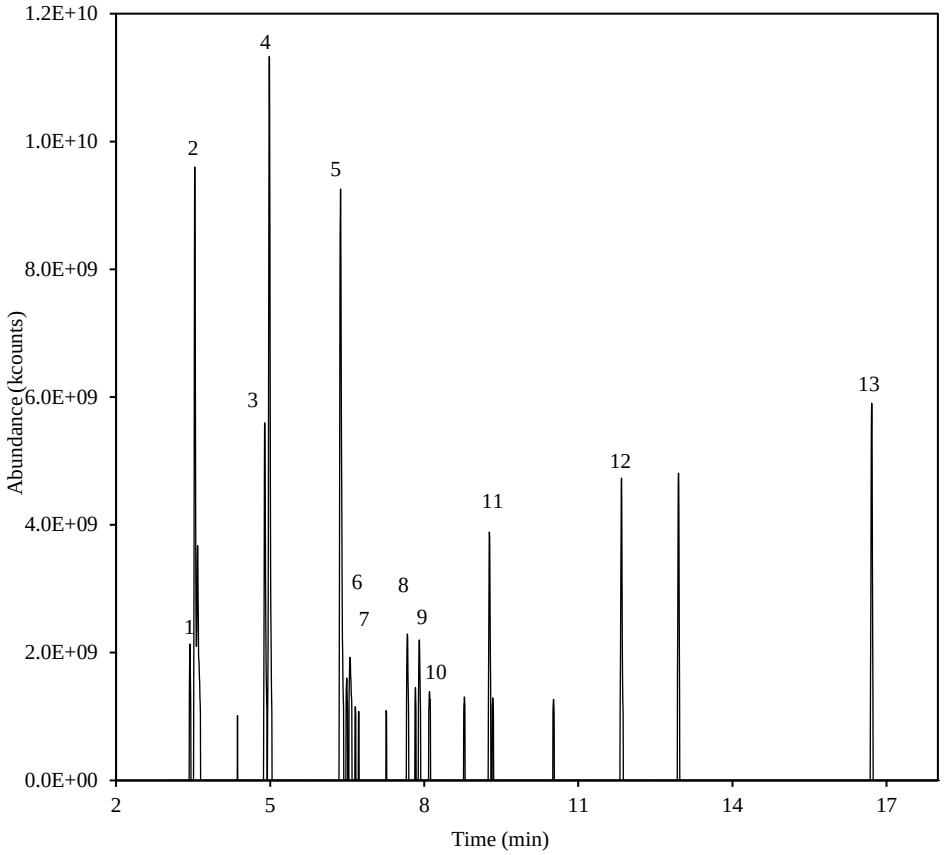

Fig. 3.3. GC/MS chromatograms of the liquid fraction obtained at 208 for 1 h.

Table 3.5. Compounds identified by CG/MS of the process water from HTC of DWAS at 208 ºC for 1 h.

Number	Compound	Molecular formula	References
1	2-Methyl-2-cyclopenten-1-one	C_6H_8O	[68]
2	1-Methyl-3-vinyl-1H-pyrazole,	$C_6H_8N_2$	
3	2-Ethyl-6-methyl-pyrazine	$C_7H_{10}N_2$	[20,68]
4	2-Formyl-4,5-dimethyl-pyrrole	C_7H_9NO	
5	3-Ethyl-2,5-dimethyl-pyrazine	$C_8H_{12}N_2$	[20,68]
6	2,5-Diethyl-pyrazine	$C_8H_{12}N_2$	[20,68]
7	2-Methyl-5-propyl-pyrazine	$C_8H_{12}N_2$	[20,68]
8	5H-5-Methyl-6,7-dihydrocyclopenta-pyrazine	$C_8H_{10}N_2$	
9	2,3-Diethyl-5-methyl-pyrazine	$C_9H_{14}N_2$	[20,68]
10	3,5-Diethyl-2-methyl-pyrazine	$C_9H_{14}N_2$	[20,68]
11	5,6,7,8-Tetrahydroquinoxaline	$C_8H_{10}N_2$	
12	2-Methyl-5-(2-propenyl)-pyrazine	$C_8H_{10}N_2$	[20,68]
13	6,7-Dihydro-2,5-dimethyl-5H-cyclopentapyrazine	$C_9H_{12}N_2$	

3.3.2. Air activation of hydrochars

The hydrochar carbonized at 208 ºC for 1 h was subjected to air-activation (300-450 ºC for 2 h) and the results are showed in Fig. 3.4. BET surface area decreased as temperature increased,

reaching values up to 99 m^2/g (325 ºC), probably due to excessive carbon burn-off, which caused the pore collapse [73–75]. Carbon content varied from 30 to 44% while the ash content increased with temperature with values in the range of 61-87%. The air-activation of DWAS (without previous HTC) was carried out as an additional experiment obtaining a carbonaceous material with a negligible BET surface area (<3 m^2/g), which justified the importance of HTC treatment previously to activation for a better control of the porous structure.

Well-carbonized hydrochars (180 ºC-4 h, 208 ºC-1 h, 208 ºC-3.5 h, and 220 ºC-2.3 h) were subjected to air-activation at 325 ºC for 2 h to analyze the importance of the carbonization conditions in the porous structure of the air-activated carbons. Fig. 3.5 shows the carbon content and BET area of air-activated hydrochars. BET areas of air-activated carbons were improved at higher HTC severity. HTC conditions, especially the temperature played a crucial role in the porous structure development of air-activated carbon materials, which confirms that the surface area and porosity can be controlled by adjusting the HTC conditions [76]. Previous works have reported that degree of aromatization and amount of condensed aromatic C increased with increasing with temperature, enhancing the structural order and chemical stability of hydrochar [77]. The greatest BET surface area (121 m^2/g) corresponded with the carbon material obtained from the hydrochar carbonized at 220 ºC for 2.3 h, with a high mesoporous contribution, while microporosity was slightly developed. These BET areas were somewhat higher than the reported for sewage biosolids pirolyzed at 750 ºC for 0.5 h [7] or air-activated at 400 ºC for 2 h (92 m^2/g) [40].

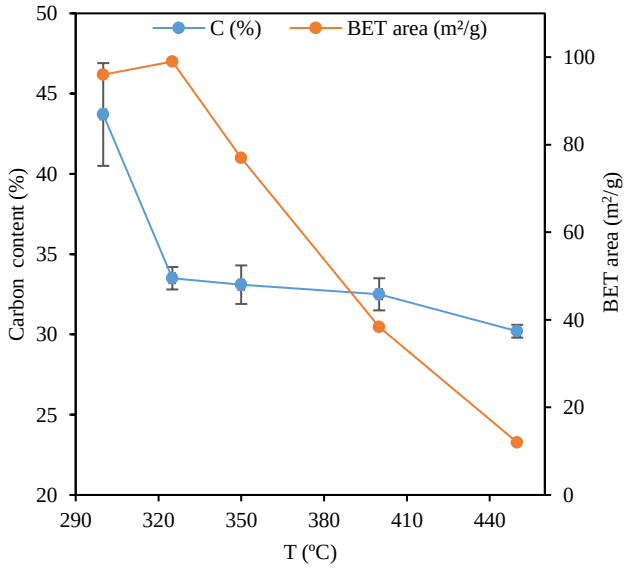

Fig. 3.4. Carbon content (ash free basis) and BET area of the hydrochar carbonized at 208 ºC for 1 h activated with air at different temperatures.

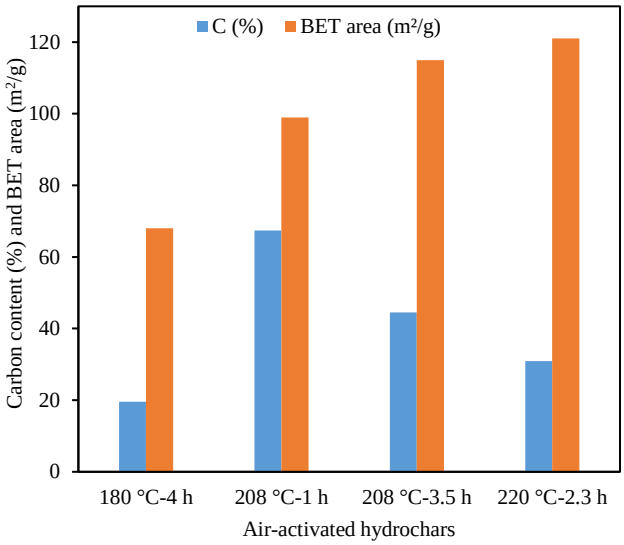

Fig. 3.5. Carbon content (ash free basis) and BET area of hydrochars activated with air at 325 ºC for 2 h.

3.3.3. Chemical activation of hydrochars

Hydrochar carbonized at 208 ºC for 1 h was chemically activated with K_2CO_3, KOH, $FeCl_3$, and $ZnCl_2$ as chemicals agents in a single-step process at 650 and 850 ºC for 1 h. Representative analysis of activated carbons obtained by chemical activation are summarized in Table 3.6.

In general BET surface area increased with the temperature except for $FeCl_3$-AC. It is worth highlighting the relatively high BET areas obtained with KOH, Na_2CO_3, and $ZnCl_2$, taking into account the high ash content of the hydrochar used as precursor (19.7% wt.). The higher BET surface areas were observed for $ZnCl_2$-AC (1030 m^2/g) and KOH-AC (968 m^2/g) activated at 850 ºC. Similar BET areas were obtained by Benstoem et al. [78] and Rodriguez et al. [79] using fibers from wastewater screenings and digestate by means of HTC and chemical activation (KOH). The hydrochars activated with $FeCl_3$ showed low surface areas (411-443 m^2/g) under the experimental conditions used, similar to the reported by Tian et al. [80] for directly $FeCl_3$-activation of cotton waste, while Bedia et al. [81] observed a higher BET area (716 m^2/g) for $FeCl_3$-activation of sewage biosolids at 750 ºC for 2 h. Micropore and mesopore volume of activated carbons were substantially increased with temperature ($V_{micropores}/V_{total}$ ~0.5) in comparison to hydrochar and the values are in agreement with the observed by Rodriguez et al. [79] and Rodriguez et al. [82] for activated carbons from hydrochars of digestate and woody biomass, respectively.

The volatile matter, ash content and fixed carbon varied from 10-27%, 9-58% and 8-67%, respectively. The C content of the ACs ranged from 29-81% and decreased as the temperature raised except for the materials activated with KOH. Sevilla et al. [83] indicated that high C content could be reached by chemical activation with NaOH. This fact is due to the release of CO_2 and CO which is favored when the activation temperature is increased, resulting in further carbon content of KOH-ACs. The hydrochars activated with KOH, $ZnCl_2$, and K_2CO_3 at 650 ºC could have potential application as absorbents because showed a well-developed porous structure, a C content (52.0-65.9%) relatively high, and ash content lower (9.4-18.0%).

Table 3.7 shows the iron and zinc distribution for the $FeCl_3$-AC and $ZnCl_2$-AC analyzed by XPS and TXRF, respectively. High iron content was found in $FeCl_3$-AC obtained at 850 ºC. Taking into account that M_{XPS}/M_{bulk} ratio closer to 1 indicate that active phase distribution is more homogeneous through the carbon particles. Thus, ACs produced with $ZnCl_2$ and $FeCl_3$ exhibited a homogenous zinc or iron distribution, respectively, except to $FeCl_3$-ACs obtained at 650 ºC which has a high iron mass concentration on their surface. Further research could be done to explore the potential of $FeCl_3$-ACs as catalyst [84].

Table 3.7. Mass concentration of iron and zinc in the $FeCl_3$-AC and $ZnCl_2$-AC prepared at 650 and 850 ºC.

Activated carbon	**T(ºC)**	**M_{XPS}(%)**	**M_{bulk}(%)**	**M_{XPS}/M_{bulk}**
$FeCl_3$-AC	650	12.6	20.7	0.6
	850	38.9	30.6	1.3
$ZnCl_2$-AC	650	3.2	3.2	1.0
	850	5.0	4.4	1.1

Table 3.6. Representative analysis of activated carbons obtained by chemical activation (composition in % wt., d.b.).

Material	T (ºC)	Volatile Matter (%)	Ash Content (%)	Fixed Carbon (%)	Elemental composition (%)					S_{BET} (m^2/g)	$V_{micropores}$ (cm^3/g)	$V_{mesopores}$ (cm^3/g)
					C	H	N	S	O[a]			
K_2CO_3-AC	650	18.8±1.0	13.1±0.5	55.0±1.3	61.1±0.6	2.2±0.1	5.8±0.3	0.2±0.1	17.6±0.3	583	0.235	0.189
	850	10.3±0.4	43.4±0.8	28.9±1.0	34.9±1.0	2.1±0.1	0.5±0.1	0.1±0.1	19.1±0.4	832	0.290	0.268
KOH-AC	650	19.1±0.8	18.0±0.5	52.0±1.4	60.9±2.7	2.0±0.1	7.4±0.2	0.7±0.1	11.0±0.4	402	0.162	0.079
	850	11.2±0.5	10.9±0.4	67.2±1.7	81.0±3.8	1.2±0.1	1.3±0.1	0.1±0.1	14.0±0.3	968	0.354	0.271
$FeCl_3$-AC	650	26.1±1.0	37.6±0.7	23.8±0.5	39.9±0.1	2.3±0.1	4.8±0.2	0.1±0.1	15.4±0.6	443	0.179	0.098
	850	26.9±0.8	58.4±1.2	7.5±0.3	28.9±0.2	1.3±0.1	1.8±0.1	0.2±0.1	9.5±0.5	411	0.136	0.146
$ZnCl_2$-AC	650	14.8±0.7	9.4±0.3	65.9±1.3	66.4±0.1	2.2±0.1	6.9±0.2	0.3±0.1	14.8±0.6	661	0.249	0.145
	850	19.4±0.6	18.6±0.6	50.1±1.6	57.6±3.0	2.1±0.1	5.3±0.2	0.6±0.1	15.7±0.7	1030	0.398	0.204

[a]By difference

3.3.4. Surface chemistry characterization by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR)

Fig. 3.6 shows the SEM images of the DWAS, hydrochar, and air-activated hydrochar. The DWAS showed a quasi-spherical structure and is virtually a non-porous solid (Fig. 3.6 a and b). Hydrochar resulting from HTC at 208 ºC for 1 h (Fig. 3.6 c and d) presented irregular shapes and developed low porosity, probably due to recondensation of volatile substances [85]. Besides, agglomerated and aggregated structures were formed by HTC in comparison with DWAS. Air-activated hydrochar (Fig. 3.6 e and f) showed major changes on the surface, which appeared to be rougher and integrated by aggregated microgranules.

Fig. 3.7 shows the SEM images of the hydrochars chemically activated at 850 ºC for 1 h. These materials, with rigid surfaces and well-developed structures, were markedly different than hydrochar and air-activated hydrochar. The material morphology was highly dependent on the activation method used. For K_2CO_3-AC (Fig. 3.7 a and b) and KOH-AC (Fig. 3.7 c and d) irregular shaped particles were observed on their surface. Also, the surface of K_2CO_3-AC was rougher than that of KOH-AC. The $FeCl_3$-AC (Fig. 3.7 e and f) presented a heterogeneous morphology and no well-developed porosity. The activation with $ZnCl_3$ originated visible and more prominent cracks, with large cavities and some micropores (Fig. 3.7 g and h).

Fig. 3.8 a shows the FTIR spectra of DWAS and several hydrochars. Four regions were selected to identify the main peaks. In the first region (3550-3150 cm^{-1}), the peak intensity at 3420 cm^{-1} was attributed to -OH stretching vibration in carboxyl or hydroxyl groups and it was found a decreased when the dehydration reaction took place [86]. In the range from 2950 to 2750 cm^{-1} named region 2, the peaks were associated with aliphatic carbon -CH_X stretching vibration. The bands appearing at 2970 and 2860 cm^{-1} were attributed to the asymmetric and symmetric –C–H stretching of the methylene groups [45]. These peaks tended to be less intense in the hydrochars probably showing the evolution of nonpolar alkyl carbon group [86]. In the band around of 1750-1300 cm^{-1} (region 3) were identified three peaks. The first peak corresponded to the stretching vibration of C=N amides at 1650 cm^{-1} [87] and the second one corresponded to -N-H in-plane bending of amide II and secondary amines (1540 cm^{-1}) [86,88]. Meanwhile, that third peak (1410 cm^{-1}), corresponded to the N-O group [45]. The signal decrease in the peaks abovementioned was probably due to the nitrogen content removal in the DWAS as HTC reaction took place. In region 4 (1200-950 cm^{-1}) a peak, approximately at 1100 cm^{-1}, was identified, which was associated with alcohol -C-O and C-O-R in aliphatic ethers stretching [89]. This peak increased with the temperature, which could confirm that the dehydration reaction of alcohol took place [87].

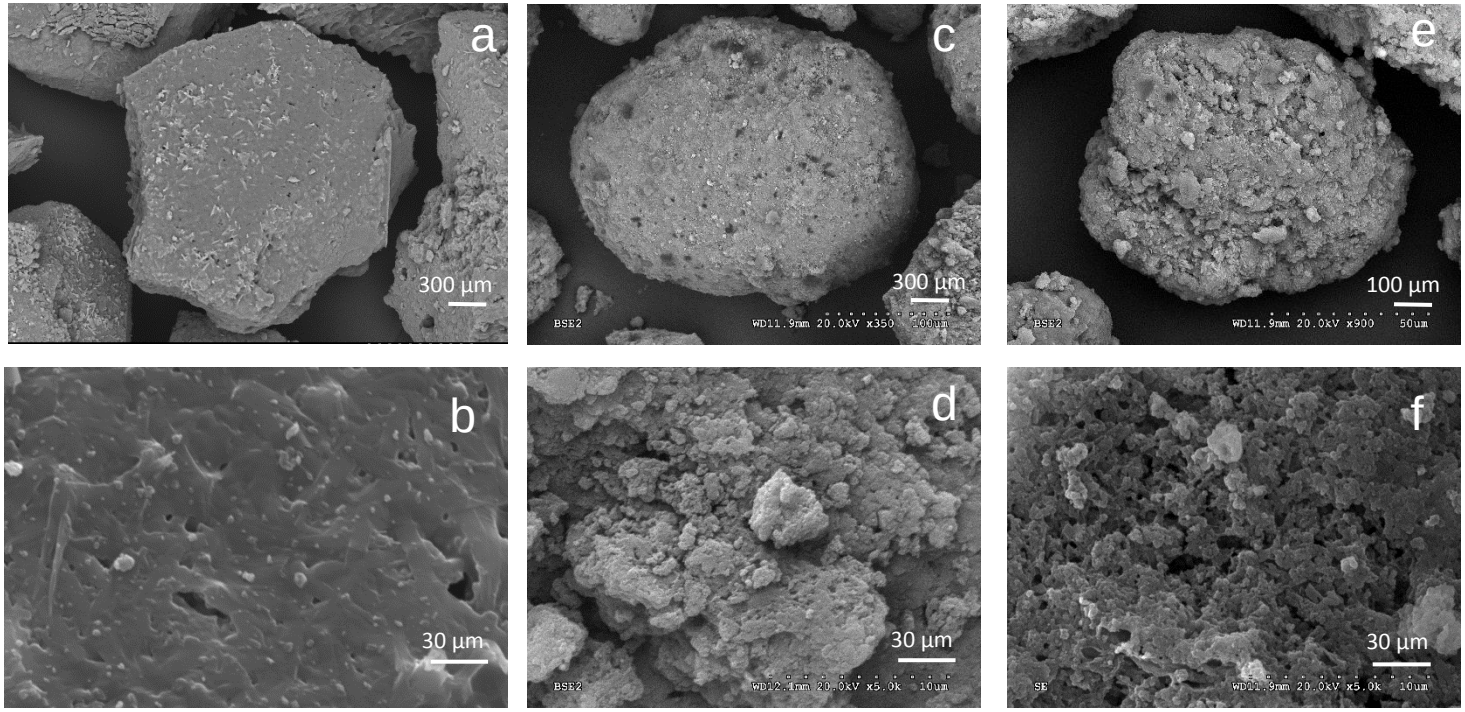

Fig. 3.6. SEM images of DWAS (a, b), hydrochar (208 ºC for 1 h) (c, d) and air-activated hydrochar (325 ºC for 2 h) (e, f).

Fig. 3.7. SEM images of K_2CO_3-AC (a, b), KOH-AC (c, d), $FeCl_3$-AC (e, f), and $ZnCl_2$-AC (g, h) activated at 850 ºC for 1 h.

Fig. 3.8 b shows the FTIR spectra for air-activated hydrochars at several temperatures. The peaks intensity at 3420 cm^{-1} was disfavored with the increase of the activation temperature. The band associated with C≡N (1650 cm^{-1}) was much more prominent for the AC obtained at 325 ºC. However, the peak -C-O and C-O-R (1100 cm^{-1}) associated with the functional group as alcohols, phenols, carboxylic acids, and esters [90] raised with the increase of the temperature. Functional groups such as carboxylic acid or carboxylic anhydride, lactone, and phenolic hydroxyl are associated with acidic surface chemistry of activated carbons [91]. The presence of surface acidic groups confers a polar character to the activated carbon surface, which can increase the adsorption capacity for polar alkaline adsorbates (i.e. ammonia, alcohol vapors and water vapor) [92,93]. Yonn et al. [94] noted that perchlorate (CO_4^-) could be absorbed on negatively charged activated carbon by R-C=OH (hydroxyl) and R-C=O groups (R represents aromatic rings). While Tsai et al. [95] stated that acid sulfonic ($-SO_3^-$) and/or phenolic groups present in acid orange 10 dyes could interact with acid groups of activated carbon.

The FTIR spectra for the chemical-activated hydrochars is showed in Fig. 3.8 c. The band associated with -OH (3420 cm^{-1}), alcohol -C-O, and C-O-R in aliphatic ethers stretching (1100 cm^{-1}) was most intense for K_2CO_3-AC compared with other materials. The production of activated carbon from hydrochar increases the presence of oxygenated functional groups including carboxylic, carbonyl and phenolic groups, which conferred unique physicochemical properties. Besides, these groups are promoted by chemical activation [36]. Due to hydrochars are more reactive that conventional chars, determined burn-off level is reached more rapidly. As a consequence, saving costs respect gases used (i.e., air, N_2) and the energy needed in the activation can be achieved [53]. Air-activated hydrochars at 400 and 450 ºC (Fig. 3.8b) showed a more intense peak at 1100 cm^{-1} than those obtained from precursors (hydrochars) and chemical-activated hydrochars.

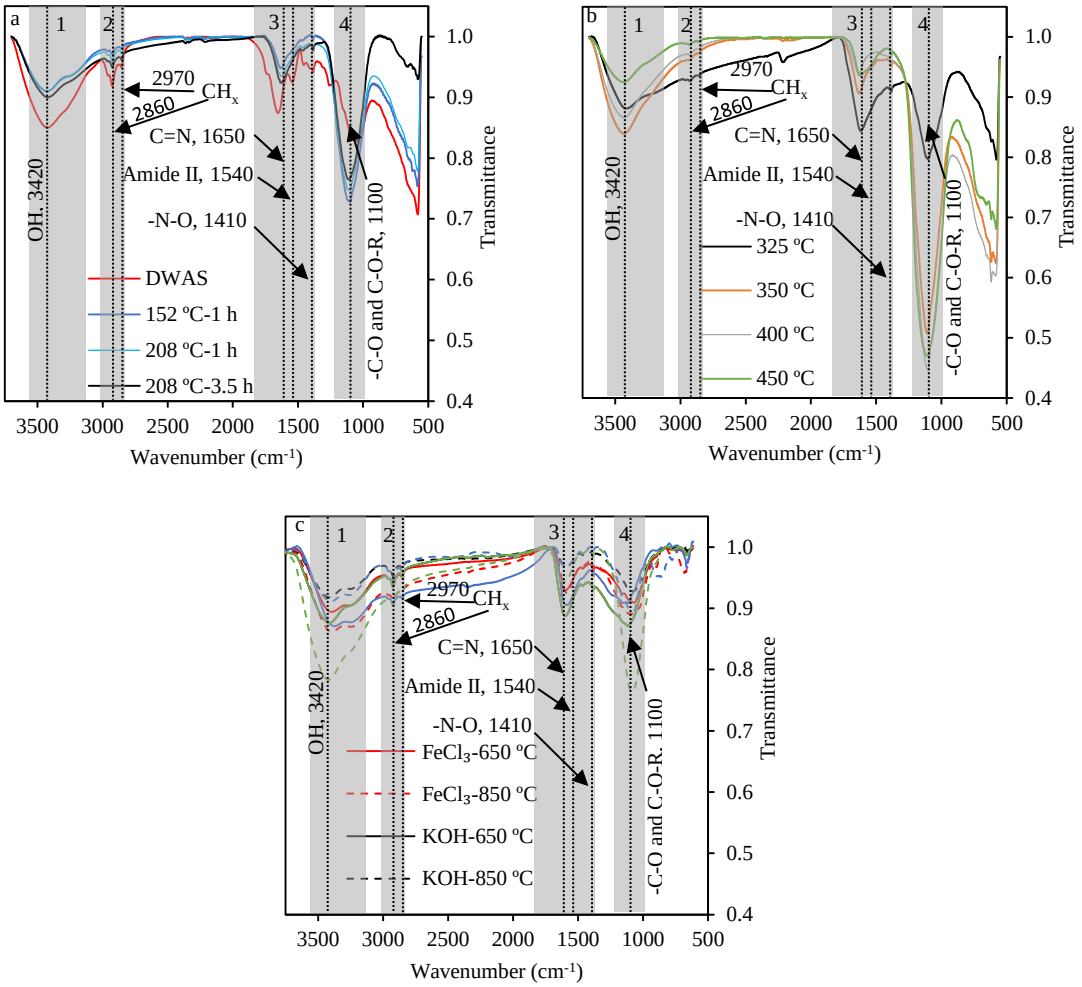

Fig. 3.8. FTIR spectra of dewatered waste activated sludge (red line) and hydrochars obtained at different temperatures and reaction times (a); air-activated carbons obtained at several temperatures (b); and chemically-activated carbons obtained at 650 and 850 ºC (c).

3.4. Conclusions

The hydrothermal carbonization can be a viable option for the valorization of dewatered waste activated sludge (DWAS) by the production of a hydrochar with similar characteristics to bituminous coal. This renewable solid fuel with high energy density can be blended with other biomass residues to improve the thermal characteristics and combustion behavior. Also, hydrochar could be used as a precursor of activated carbons with oxygenated functional groups that conferred unique textural and surface properties. HTC of DWAS followed by air activation produced activated carbon with moderate surface area and tunable surface chemistry, while activated carbons with relatively large surface area and fairly different porous structure were obtained using HTC followed by chemical activation, with potential application as absorbents or catalytic supports.

Due to NPK content and micronutrients present in the process water from HTC, it could be used as a supplemental fertilizer. Further research might explore the potential of this HTC liquor for nutrient recovery such as phosphorus and nitrogen.

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Chapter 4:

Valorization of the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge by mesophilic anaerobic digestion in batch experiments

4.1

Valorization of the liquid fraction from hydrothermal carbonization of sewage sludge by anaerobic digestion

J.A. Villamil, A.F. Mohedano, J.J. Rodriguez, M.A. de la Rubia, Valorization of the liquid fraction from hydrothermal carbonization of sewage sludge by anaerobic digestion, J. Chem. Technol. Biotechnol. 93 (2018) 450–456

Abstract

The mesophilic anaerobic digestion of the liquid fraction from hydrothermal carbonization (208 ºC for 1 h) of dewatered waste activated sludge, has been studied. Two initial inoculum concentrations (IC) (10 and 25 g COD/L) and four inoculum to substrate ratios (ISR) (2, 1, 0.5 and 0.4 on a COD basis), have been selected to analyze their influence on the evolution of the anaerobic digestion process. The substrate is characterized by a high COD (95.5 g/L) and TKN (8.7 g N/L) values. High inoculum concentration (25 g COD/L) and/or low ISR (≤0.5) inhibited the methanogenesis due to the high ammonia nitrogen (1.4 g TAN/L) and VFA (>4 g COD/L) released. For the inhibited samples, COD removal lower than 15% and IA/TA ratios higher than 0.3 were found. The greatest methane yield (177±5 mL STP CH_4/g COD_{added}) was achieved at 25 g COD/L of IC and at an ISR of 2. During the anaerobic digestion of the liquid fraction from the hydrothermal carbonization of dewatered waste activated sludge, the IC and ISR must be adequately selected for a proper operation of the process and a successful valorization. According to the results, working at an ISR≥1 is recommended.

4.1.1. Introduction

Wastewater treatment plants (WWTP) generate huge amounts of sewage sludges which are currently managed through agricultural application, incineration or landfilling. In this context, different methods of thermal valorization, such as pyrolysis or gasification, are being investigated in the last two decades [1]. As an alternative to these methods, hydrothermal carbonization (HTC), a relatively new process for biomass carbonization, usually performed at 180–375 ºC under auto-generated pressures [2], has been gaining attention, because energy-intensive predrying is not necessary [3]. Moreover, the hydrochar (HTC char) has a higher heating value compared to the biochar produced from slow-pyrolysis or conventional carbonization at the same temperature [4]. Hydrochar has several industrial and environmental applications such as soil remediation, solid fuel and CO_2 sequestration [5,6]. The char obtained via HTC is a slurry that needs to be separated through filtration. Most of the studies of HTC have been focused on the optimization of the reaction conditions to obtain solid fuels [3,7]. Depending on the process conditions, the HTC liquor can contain up to 15-20% of the initial carbon, mainly in the form of formic and acetic acids, sugars, nutrients and other compounds [8,9]. Also, the formation of recalcitrant or inhibitory compounds such as furfural, phenols and furan may occur during the hydrothermal process [10,11]. Therefore, that liquid fraction has much higher

total chemical oxygen demand (TCOD) than most types of organic wastewaters. Besides, the HTC conditions (temperature and time) affect to that TCOD. Values around 60 g/L have been reported from HTC of food waste or orange pomace [12,13] and somewhat lower values (40-50 g/L) have been obtained from agro-industrial residues like chaff, corn silage or thin stillage [14-16], while for HTC of primary sewage, mixture of primary and secondary sludge and digested municipal sewage sludge, values of 23, 52.5 and 34 g/L have been, respectively, reported [2,17,18]. Therefore, the liquid fraction from HTC, needs to be conveniently managed before final discharge and moreover its high organic load offers potential interest for the sake of valorization. Different solutions have been proposed, including the use as feedstock for chemical production [19] recycling in consecutive HTC runs to improve the carbon yield or biological stabilization [9,20]. Chemical and biological treatments have been evaluated for the liquid fraction from HTC of sewage sludge. Wet air oxidation allowed reducing total organic carbon (TOC) up to 60% [21]. Ramke et al. [22] reported COD reduction over 85% upon aerobic degradation. Anaerobic digestion of that liquid fraction has been suggested as a potential route to optimize energy recovery [23,24]. However, the potential to produce methane from the liquid fraction of HTC has been scarcely studied and the existing information deals mainly with lignocellulosic residues [13,14,16,25]. Qiao et al. [17] determined the biogas and methane production of the supernatant obtained from HTC of municipal sludge. Danso-Boateng et al. [2] used experimental data of COD from the liquid fraction of the hydrothermal carbonization of sewage sludge to estimate theoretical methane yields. The aim of this study is to analyze the potential valorization of the liquid fraction from hydrothermal carbonization of sewage sludge by anaerobic digestion. For that purpose, the initial inoculum concentration (IC) and the inoculum to substrate ratio (ISR) have been checked as main variables. Two IC values (10 and 25 g COD/L) and four ISR (2, 1, 0.5 and 0.4, in terms of COD) were tested. So far, only few studies can be found in the literature relative to the effect of those two variables on the evolution of singular parameters of anaerobic digestion: pH, volatile fatty acids (VFA), alkalinity, ammoniacal nitrogen, COD and methane potential. The anaerobic digestion experiments were performed in batch-wise.

4.1.2. Materials and methods

HTC experiments and substrate characteristics

A dewatered waste activated sludge (DWAS) with 85% moisture was collected from a full-scale membrane bioreactor treating industrial wastewaters from a cosmetics factory. It was maintained at -20 ºC until use. HTC was performed at 208 ºC for 1 h in a ZipperClave® pressure vessel electrically heated using 1.5 kg of DWAS. The final temperature was reached at a heating rate of 3 ºC/min. The reaction was stopped by cooling in a heat exchanger using tap water. The liquid fraction (LF) was recovered by centrifugation (3500 rpm for 1 h) and filtration (0.45 µm) being then maintained at 4 ºC until batch anaerobic digestion were performed.

The main characteristics and composition of this liquid fraction LF from HTC were as follows (average values of three determinations with standard deviations): pH: 5.1±0.1, soluble COD (SCOD): 95.5±0.4 g O_2/L, total solids (TS): 51.9±0.5 g/L, volatile solids (VS): 46.2±0.5 g/L, biochemical oxygen demand (BOD_5): 25.6±1.1 g/L, TOC: 42.6±0.9 g/L and total Kjeldahl nitrogen (TKN): 8.7±0.1 g N/L. The analysis by HPLC/RI allowed determining the concentration of formic, acetic, iso-butyric and butyric acid, which yielded values of 1420±20 mg/L, 2269±33 mg/L, 930±11 mg/L and 94±4 mg/L, respectively.

Inoculum source

The inoculum was a granular anaerobic sludge from an industrial digester treating brewery wastewater under mesophilic conditions (35 ºC). Its main characteristics were: pH: 7.6±0.1, TS: 61.9±0.9 g/L, VS: 55.7±0.9 g/L, TCOD: 91.2±1.4 g O_2/L and TKN: 2.2±0.1 g N/L.

Experimental set-up and procedure

Anaerobic digestions runs were carried out in 120 mL glass serum vials, filled with 60 mL of a suspension of inoculum, substrate and a basal medium with macronutrients (NH_4Cl, 280 mg/L; K_2HPO_4, 250 mg/L; $MgSO_4 \cdot 7H_20$, 100 mg/L; $CaCl_2 \cdot 2H_2O$, 10 mg/L; yeast extract, 100 mg/L) and micronutrients ($FeCl_2 \cdot 4H_2O$, 2 mg/L; $CoCl_2 \cdot 6H_2O$, 2 mg/L; 0.5 $MnCl_2 \cdot 4H_2O$, mg/L; $AlCl_3 \cdot 6H_2O$, 0.09 mg/L; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.05 mg/L; H_3BO_3, 0.05 mg/L; $ZnCl_2$, 0.05 mg/L; $CuCl_2 \cdot 2H_2O$, 0.038 mg/L) as it is recommended [26]. Before sealing the vials with rubber stoppers and metallic crimps, the suspensions were flushed with N_2 for 3 min. The vials were placed in a static incubator at mesophilic

temperature (35±1 ºC) and were daily mixed. Table 4.1.1 describes the experimental conditions used in these batch anaerobic digestion experiments. As indicated before, two IC values (10 and 25 g COD/L) and four different ISR (0.4, 0.5, 1 and 2, on a COD basis) were tested. The experimental period was extended until the methane production was undetectable or less than 5% of the total produced (on the last day).

For every inoculum concentration three blank runs (for subtracting the methane production due to biomass decay and the possible presence of residual substrate in the inoculum) and three positive controls (tests with starch as only substrate) were carried out (these control yielded approximately 350 mL STP CH_4/g COD_{added}). For each of the 8 conditions tested (Table 4.1.1), 9 batch reactors were ran. Six of them were sacrificed and removed every one or two days initially and then weekly in order to study the time-course of the anaerobic digestion process. The other three reactors were used only for biogas analysis (volume and composition).

Table 4.1.1. Experimental conditions and notation of the anaerobic digestion experiments.

	Inoculum	**Substrate**			
ISR on a COD basis		2	1	0.5	0.4
ISR on a VS basis		2.6	1.3	0.6	0.5
Concentration (g COD/L)	10	5.0	10.0	20.0	25.0
NOTATION in the text		1-2	1-1	1-0.5	1-0.4
Concentration (g COD/L)	25	12.5	25.0	50.0	62.5
NOTATION in the text		2.5-2	2.5-1	2.5-0.5	2.5-0.4

Analytical methods

The inoculum was characterized by measuring the pH (using a model Crison 20 Basic pH-meter), TS and VS, according to the standard methods 2540B and 2540E, respectively [27]. The TCOD was determined by the method proposed by Raposo et al. [28]. TKN was determined acidifying 1000 mg of sample with 15 mL of concentrated H_2SO_4 (85% wt.). In addition, 5 g of catalyst [(Cu–Se) (1.5% $CuSO_4 \cdot 5H_2O$+2% Se)] were added, and the sample was digested sequentially in a thermoblock for 15 min at 150 ºC, 15 min at 250 ºC and 90 min at 390 ºC and then distilled and titrated according to the standard method 4500E [27].

The LF from HTC, as well as the sacrificed samples (centrifuged and filtered through a 0.45 µm filter) were used to determine the following parameters: pH; partial and total alkalinity (PA and TA, by pH titration to 5.75 and 4.3, respectively [29]; intermediate

alkalinity (IA, defined as the difference between TA and PA); SCOD (using the closed digestion and colorimetric standard method 5220D [27]; TOC (measured with an automatic analyser TOC-VCPN, Shimadzu); TKN; total ammonia nitrogen (TAN), determined by distillation and titration according to the standard method 4500E [27]; free ammonia nitrogen (FAN, according to Hansen et al. [30]); individual VFA were quantified by HPLC coupled with a refraction index detector (HPLC/RI, Varian, Agilent Technologies, Santa Clara, CA, USA) using a sulfonated polystyrene resin in the protonated form (67H type) as the stationary phase (Varian Metacarb 67H 300 mm) and sulfuric acid (0.0125 mol/L in milliQ water) as the mobile phase at a flow rate of 0.8 mL/min. Column temperature was 65 ºC [31]. Gas chromatography/ion trap mass spectrometry (GC–MS; CP-3800/Saturn 2200 using a Varian CP-8200 autosampler injector, and a solid phase microextractor, Carbowax/Divinylbenzene Yellow-Green to identify chemical species). The capillary column used was a Factor Four VF-5ms (30 m long, 0.25 mm diameter). Sample injection was carried out with split-less at 220 ºC, using He as carrier gas. The temperature program used in the GC/MS analyses ramped as follows: 40 ºC for 15 min and 15 ºC/min until 250 ºC. The compounds were assessed using the NIST 2008 Library.

Biogas and methane production were measured once every day during the first 3 days and eight more times for the rest of the incubation period. Biogas production was determined by manometric method [32], measuring the pressure increase in each vial by an electronic pressure monitor (ifm, PN 7097). It was expressed at standard temperature and pressure (STP: 273K, 1bar) conditions. Biogas was subsequently exhausted to re-establish atmospheric pressure. Methane production was calculated by subtracting the amount of methane produced in the blank controls from the methane production of each batch reactor. The gas composition (H_2, CO_2 and CH_4) was determined by gas chromatography using a Bruker 450-GC (Goes, The Netherlands) coupled with a thermal conductivity detector (TCD) for H_2 and CO_2 and a flame ionization detector (FID) for CH_4 [31].

4.1.3. Results and discussion

Anaerobic digestion process

The initial and final values of pH, total alkalinity and IA/TA ratio from the anaerobic digestion experiments are collected in Table 4.1.2. The initial pH was higher than 7 for samples with an ISR≥1, but lower for the rest, even lower than 6 for samples 2.5-0.5 and 2.5-0.4. The pH of the HTC liquid fraction was acidic (5.1±0.1), in agreement with the

observed by other authors [22,25]. In all the cases the pH increased during the anaerobic process. It has been stated that values lower than 6.5 can provoke methanogenic inhibition [33]. The initial total alkalinity for the tests developed at 10 g COD/L of IC value, ranged between 1 and 2 g $CaCO_3$/L, being significantly higher for the runs at higher concentration (25 g COD/L). The final alkalinity values increased around twofold in all cases, from 2.2 (run 1-2) to 9.50 (run 2.5-0.4) g $CaCO_3$/L. Alkalinity values above 2.5 g $CaCO_3$/L provide a buffering capacity, so that even a large increase of VFA reduces only minimally the pH [34]. Looking at those values it would seem that the anaerobic process performed stably and well buffered. However, except for the samples 1-2, 1-1 and 2.5-2, the starting intermediate to total alkalinity ratio was higher than 0.3, which is not recommended for a good stability of the anaerobic process [35].

Table 4.1.2. Values of pH, alkalinity and intermediate to total alkalinity ratio from the anaerobic digestion experiments.

Experiment	**pH**		**Alkalinity (g $CaCO_3$/L)**		**IA/TA**	
	Initial	Final	Initial	Final	Initial	Final
1-2	7.5	7.7	1.02	2.19	0.32	0.26
1-1	7.3	7.9	1.46	3.78	0.51	0.21
1-0.5	6.5	7.0	1.81	4.10	0.80	0.76
1-0.4	6.1	6.9	1.98	4.56	0.88	0.80
2.5-2	7.6	8.0	2.31	5.36	0.38	0.29
2.5-1	7.0	7.5	2.85	5.95	0.67	0.70
2.5-0.5	5.5	7.4	2.78	7.27	1.00	0.79
2.5-0.4	5.4	7.5	4.33	9.49	0.83	0.78

Fig. 4.1.1 shows the time-course of TVFA under the different experimental conditions tested. TVFA concentration decreased along the experimental period in 1-2, 1-1 and 2.5-2 runs. For the rest of the experiments TVFA concentration decreased during the first 1-2 days, due to the degradation of short-chain fatty acids present in the substrate, which were easily degraded. Beyond that time the TVFA concentration increased until the 10^{th}-15^{th} day due to the acidification of the complex organic matter presents in the substrate and then remained more or less stable. As it is well known, the accumulation of intermediate products, such as VFA, is indicative of process unbalance. The amount of VFAs produced increased at increasing IC and decreasing ISR values, reaching values around 9 g/L (2.5-0.5, 2.5-0.4). Silvestre et al. [36] observed strong inhibition at VFA concentrations above 5 g/L, although the collapse of the system commonly occurs at

around 10 g/L [37]. Therefore, it is clear that the pH cannot provide by itself information on imminent failure, because in medium or well-buffered solutions high VFA concentration can develop without appreciable pH decrease. Thus, direct measurements of VFA, alkalinity and in particular the IA/TA, are necessary [38].

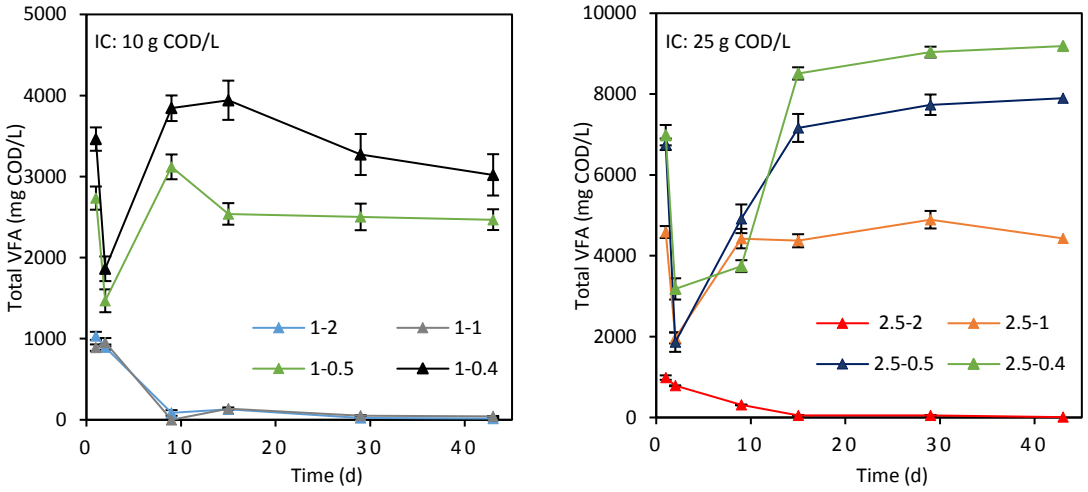

Fig. 4.1.1. Time-course of total VFA at different inoculum concentrations and ISR values.

The time-course of TAN is depicted in Fig. 4.1.2, which includes also tables with the initial TKN values. TAN reached above 80% of TKN in 1-2, 2.5-2 and 1-1 runs. The rest of experiments showed lower nitrogen hydrolysis (approximately 65-70%) and for the 2.5-0.4 condition only 46% took place. However, final TAN values for these experiments were above 1400 mg N/L. Ammonium represents an essential nutrient for microorganisms and contributes to the stabilization of pH. Ammonium bicarbonate buffers the system allowing to operate even at high VFA concentrations. However, FAN is highly toxic, especially to acetoclastic methanogens [39]. Increasing the pH displaces the ammonium/ammonia equilibrium towards the second. At 35 ºC and pH lower than 7, TAN is almost completely in the form of ammonium, and at pH 8 only around 10% is as FAN. The highest FAN concentration was observed in the 2.5-1 experiment, with 125 mg NH_3/L, substantially below than the 700-1100 mg NH_3/L range reported to cause strong inhibition [40]. In the case of TAN, inhibiting values between 1500 and 7000 mg N/L have been reported [41]. Thus, operational difficulties through inhibition of the methanogenic Archaea because of TAN accumulation may occur clearly at the highest IC value tested and at an ISR<2 (experiments 2.5-1, 2.5-0.5 and 2.5-0.4), and also at the lowest IC when ISR<1 (1-0.5 and 1-0.4).

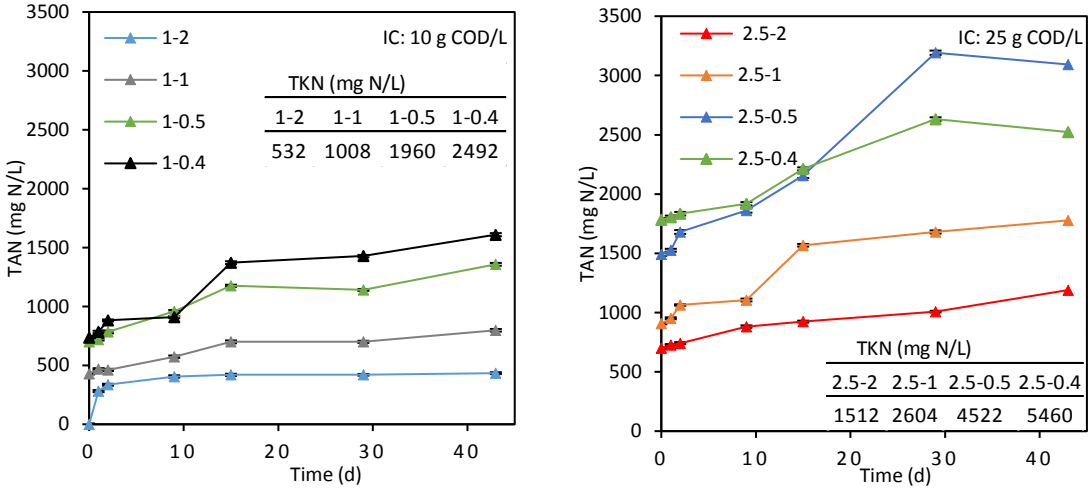

Fig. 4.1.2. Initial TKN values (tables) and time-course of total ammonia nitrogen at different inoculum concentrations and ISR values.

The initial substrate concentration ranged from 5 to 62.5 g O_2/L of COD, with proportionally higher values as the digesters were more heavily loaded. Initially, the SCOD values increased in each experiment up to 6.8 and 68.5 g O_2/L, respectively (Fig. 4.1.3) as the result of inoculum hydrolysis. COD removal was negligible for 2.5-1 and 1-0.4 runs (2-4%), while the highest reductions were observed in the 1-2, 1-1 and 2.5-2 experiments (38-44.5%). Final COD attributable to VFA was less than 20% for the experiments carried out at an ISR≤1. Therefore, above 80% of the final COD in those experiments is due to other refractory compounds which accumulate in the reactor inhibiting the anaerobic process.

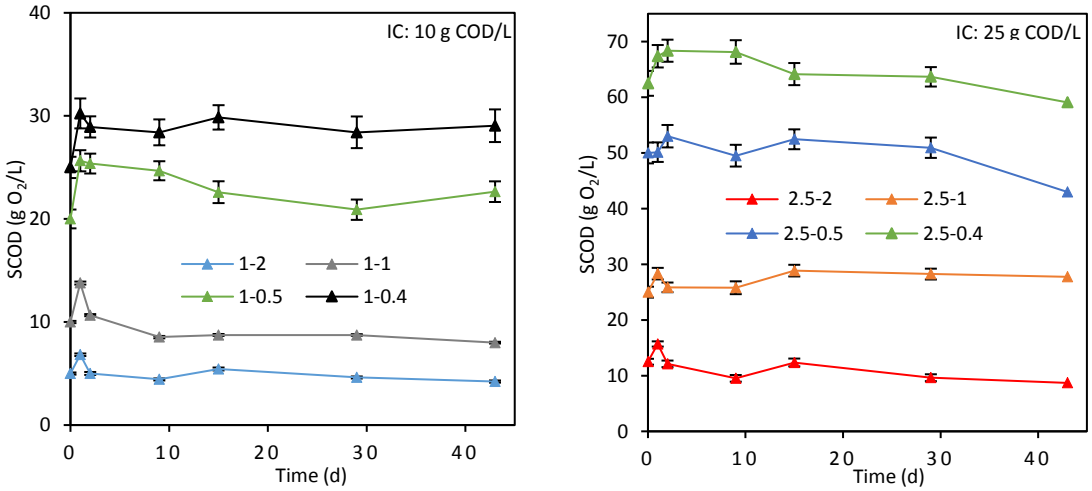

Fig. 4.1.3. Time-course of soluble COD at different inoculum concentrations and ISR values.

Phenolic and aromatic compounds were identified in the starting HTC liquid. This is consistent with a common carbonization route including hydrolysis, dehydration,

decarboxylation, condensation, polymerization and aromatization reactions as previously reported by Danso-Boateng et al. [2]. Products such as aldehydes, furans, pyrroles, pyrazines, and pyridines were also detected. The high concentration of TKN can be due to the presence of several nitrogen-containing species that may have relatively high molecular weight. Anaerobic digestion led to almost complete removal of the furan (furan, 2,5-dimethyl-) and aldehyde (4-methoxycinnamaldehyde) species present in the initial HTC liquid, but a new aldehyde compound (2,3,6- trichlorobenzaldehyde) appears as a degradation intermediate in the experiments at the lowest IC value (1-2 and 1-1) (Table 4.1.3.).

Table 4.1.3. Compounds identified by GC/MS in the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge and removal efficiencies upon anaerobic digestion.

Compound	**Removal efficiency (%)***		
	2.5-2	1-2	1-1
Aldehydes			
4-Methoxycinnamaldehyde	>99	>99	>99
2,3,6-Trichlorobenzaldehyde	nd	gen	gen
Nitrogenatescompounds			
4-Pentyloxyaniline	>99	>99	>99
1H-Pyrrole-2-carboxaldehyde,1-methyl-	0	>99	0
Pyrazine, 2-ethyl-5-methyl-	0	0	0
Benzenamine, 3-methoxy-	0	0	9
4,5-Dimethyl-ortho-phenylenediamine	0	0	34
2,3-Diethylpyrazine	0	0	13
Pyrazine, 2,5-dimethyl-3-propyl-	15	0	45
2(1H)-Quinoxalinone	>99	>99	>99
1-Butanamine	>99	>99	>99
1H-Indole, 7-methyl-	gen	nd	nd
Oxygenated aromatics			
Furan, 2,5-dimethyl-	>99	95	>99
Benzene, 1,2,4,5-tetramethyl-	0	0	22
Phenol, 2,3,5,6-tetramethyl-	25	13	35
Benzoic acid, 4-formyl-	20	10	30
Phenol, 2-methyl-6-(2-propenyl)-	12	>99	26
Phenol, 2-methyl-5-(1-methylethyl)-	>99	>99	>99
Benzophenone	>99	>99	>99
Phenol, 2,4-bis(1,1-dimethylethyl)-	gen	gen	gen

*with respect to peak area
nd: not detected
gen: generated

Phenols and other oxygenated aromatics compounds were partially removed, whereas, most pyrazines and aromatic amines (pyrazine, 2-ethyl-5-methyl-; 2,3-diethylpyrazine; pyrazine, 2,5- dimethyl-3-propyl-; benzenamine, 3-methoxy-; 4,5-dimethyl-ortho-phenylenediamine) were refractory. Some compounds (1H-indole, 7-methyl-) not found in the initial substrate were detected in the final samples after anaerobic digestion, which may correspond to refractory intermediates. The presence of refractory species, may affect to the methane yield by limiting the efficiency of the biological process [42,43]. The presence of enough microorganisms may restrain the inhibitory effect of such species, thus explaining the higher methane production at the highest ISR.

Methane potential yield

Fig. 4.1.4 shows the cumulative methane yield along the anaerobic digestion experiments. Methane production began immediately in assays 1-2, 1-1 and 2.5-2, reaching final figures of 144±1, 158±4 and 177±5 mL STP CH_4/g COD_{added}, respectively. These yield values are lower than the observed for the anaerobic digestion of the liquid fraction from HTC of agricultural residues like thin stillage or orange pomace, where 300 and 213 mL STP CH_4/g COD, were reported, respectively [13,16], or mixed sewage sludge, with 257 mL CH_4/g COD [17], but fairly similar to the obtained by Weiner et al. [14] for the liquid fraction from HTC of chaff using organosolv as the liquid source for carbonization (174±9 mL CH_4/g COD) or by Wirth et al. (2015) [18] for the liquid fraction from HTC of digested sewage sludge as sole substrate operating in continuous feed mode (120-180 mL STP CH_4/g COD_{added}). For all the other conditions tested, inhibition of the methanogenic stage occurred, suggesting that not only the ISR but also the IC affect to methane production. At an ISR below 1 (runs 1-0.5, 1-0.4, 2.5-0.5, 2.5-0.4) and even at 1 for the highest IC (2.5-1), overload takes place, due to the increased availability of easily hydrolysable material in the reactor, which in turn leads to VFA and TAN accumulation, low COD removal, IA/TA ratios ≥ 0.75 and ultimately methanogenesis inhibition. ISR of 0.5 (on a VS basis) have been reported to inhibit methane production in anaerobic digestion of winery waste, microcrystalline cellulose production wastewater and piggery slaughterhouse [42,44,45].

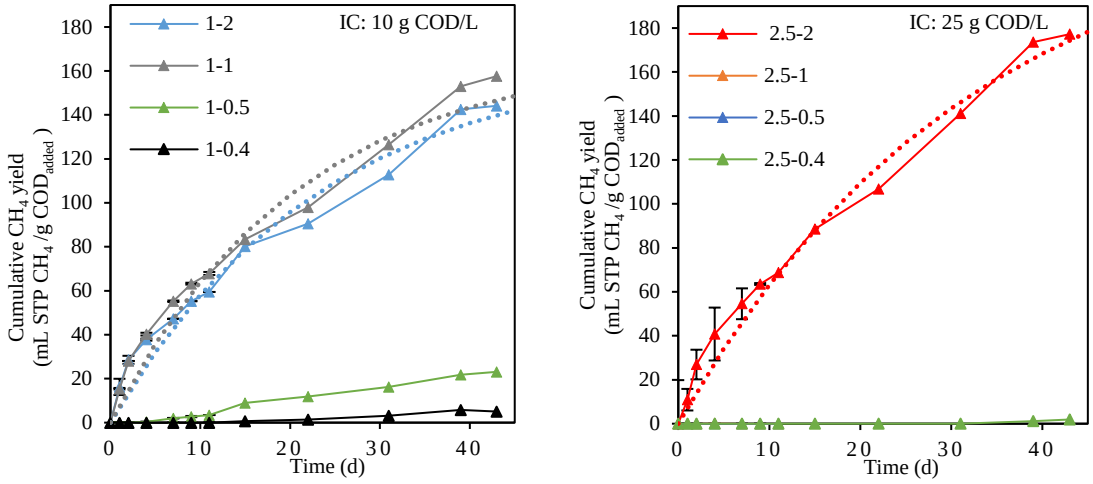

Fig. 4.1.4. Cumulative methane yield (symbols) at different inoculum concentrations and ISR values. The dotted lines show fittings to the rate equation (Eq. 4.1.1).

The results of the three experiments giving significant methane yields (1-2, 1-1 and 2.5-2), were fitted to a first-order rate equation which is a simple and useful model that has been frequently applied to anaerobic digestion systems [42-44]. The basic equation is:

$$G = Gm \cdot [1 - \exp(-k \cdot t)] \quad \text{Eq 4.1.1}$$

where G represents the cumulative methane yield at a time t, G_m is the ultimate methane yield of the substrate analyzed and k the specific rate or apparent kinetic constant. The ultimate methane yield corresponds to the final value when no more gas is released from the reactor. This equation has been frequently applied to anaerobic digestion [46]. Samples of ISR≤0.5 showed almost complete inhibition and therefore were not considered.

Origin software (version 8.0) was used to fit the experimental data to Eq. 4.1.1. Table 4.1.4 collects the values obtained for k and Gm (95% confidence), as well as the corresponding determination coefficient (R^2). This simple kinetic approach allows a good prediction of the experimental results, as can be seen in Fig. 4.1.4. The values of the apparent kinetic constants are related to the concentration of the inoculum. The highest ones (0.048±0.008 d^{-1} and 0.043±0.008 d^{-1}) were obtained for the experiments performed at the lowest concentration tested (1-1 and 1-2, respectively). Meanwhile increasing that concentration led to significantly higher G_m values.

Table 4.1.4. Values of the apparent kinetic constant (k) and maximum methane yield (Gm).

Experiment	G_m (mL CH_4/g COD_{added})	k (d^{-1})	R^2
1-2	166±17	0.043±0.008	0.966
1-1	168±14	0.048±0.008	0.972
2.5-2	237±18	0.031±0.003	0.978

4.1.4. Conclusions

Methane production from the LF from HTC of DWAS via mesophilic anaerobic digestion is a promising approach. The substrate is characterized by high COD and TKN contents, requiring adequate selection of the IC and ISR for a proper operation of the process. High inoculum concentration (25 g COD/L) and/or low ISR (≤0.5) affect negatively the ultimate methane yield through methanogenesis inhibition due to the high ammonia nitrogen and VFA released. According to the results, working at an ISR≥1 is recommended for the valorization of the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge by mesophilic anaerobic digestion.

4.1.5. References

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4.2

Effect of inoculum source and initial concentration on the anaerobic digestion of the liquid fraction from hydrothermal carbonization of sewage sludge

M.A. De la Rubia, J.A. Villamil, J.J. Rodríguez, A.F. Mohedano, Effect of inoculum source and initial concentration on the anaerobic digestion of the liquid fraction from hydrothermal carbonisation of sewage sludge, Renew. Energy. 127 (2018) 697–704

Abstract

Hydrothermal carbonization (HTC) is a relatively new alternative for the management of sewage sludge that allows obtaining a HTC char (hydrochar) with a high higher heating value (≈22 MJ/kg). The aim of this work has been to study the anaerobic digestion of the liquid fraction (LF) generated as by-product during HTC of dewatered waste activated sludge (DWAS), to get more value to the overall process. For this purpose, three different inocula: granular biomass from industrial reactors treating brewery and sugar beet wastewaters and a flocculent biomass from a full-scale digester of municipal sewage sludge at two initial inoculum concentrations (IC) (10 and 25 g COD/L) were tested. ANOVA test was applied to evaluate the ultimate methane yield for each IC. The effect was different for each inoculum studied: an increase from 10 to 25 g COD/L increased the methane yield by 23% for brewery waste, achieving the highest value obtained (177±5 mL STP CH_4/g COD_{added}), while declining to 99±2 mL STP CH_4/g COD_{added} for sugar beet; it is not affected by the municipal sludge, yielding around 135 mL STP CH_4/g COD_{added}. Therefore, among the inocula tested, brewery waste was the most appropriate for the anaerobic digestion of the LF of DWAS at high IC.

4.2.1. Introduction

Currently, farmland utilization, incineration and landfilling are the main methods for sewage sludge biosolid (stabilised sewage sludge) disposal [1]. In the last decades, thermal valorisation of sewage sludge, including pyrolysis and gasification, has been gaining attention [2,3]. Hydrothermal carbonization (HTC) is a thermochemical process for converting organic feedstock with high moisture into a carbon-rich solid product (HTC char or hydrochar) with a higher heating value compared to the biochar produced from conventional carbonization at similar temperatures [4-6]. This thermal process is performed under relatively low temperatures (180–375 ºC) and auto-generated pressure for variable lengths [7], turning out to be an attractive option for dewatered waste activated sludge (DWAS) valorization. The product from HTC of biomass is a slurry that can be separated into a solid and a liquid fraction. This liquid fraction (LF) contains at least 15% of the initial carbon content [8] and can be used as potential source of chemicals or fuels through the biorefinery concept [9]. It can also be subjected to aerobic degradation [10,11], wet air oxidation [12] or anaerobic digestion [13-23], the last being a potential route of valorization towards biogas production.

To establish the interest of using a given feedstock for anaerobic digestion, batch tests can be performed to determine the methane potential, i.e., the maximum methane quantity

that can be potentially produced. To optimize anaerobic digestion, different parameters related to the substrate, the inoculum and the operating conditions need to be checked, with the inoculum source and the inoculum to substrate ratio (ISR) being the most relevant [24-26].

The inoculum determines the initial activity of the microorganisms used for the test. Therefore, successful start-up and operation of anaerobic reactors require a seed sludge with a well-balanced microbial community [27-28]. During the process, it is expected that the microbial communities can adapt because of the growth of microorganisms under the specific digestion conditions and the substrate treatment [29]. Different inocula sources have been checked, including sludge from anaerobic digesters treating municipal or agro-industrial wastewater, animal manures and landfill leachate, among others [29-34].

Selection of the ISR is a determining issue for correct operation of anaerobic digestion. It depends largely on the substrate used, considering the potential amount of nitrogen ammonia and volatile fatty acids (VFA) produced from the hydrolysis of total Kjeldahl nitrogen (TKN) and the acidification of the organic matter, respectively [24]. Values of approximately 2 have been usually recommended [20,25,26,35], although in some cases, lower values have been successfully used [36-38]. The aim of this work is to study the valorization of the by-product (liquid fraction) generated from HTC of dewatered waste activated sludge. The hydrothermal carbonization could be a very suitable process to transform dewatered waste activated sludge into a peat-like material without pre-drying the biomass input, in a new concept for sewage management. The energetic balance is more favourable than for thermal alternative processes, converting biomass as a whole [4,39-41]. With the purpose of completing the process, the liquid fraction from HTC could be treated with the raw wastewater or co-digested with the primary sewage sludge. The potential to produce methane of this liquid by-product separated from the hydrochar has been scarcely studied so far. Hence, a more in-deep study of the anaerobic digestion of the HTC by-product is required in order to evaluate the best conditions for optimizing methane yield. Batch tests have been carried out to determine the ultimate methane yield and the evolution of key parameters during the anaerobic digestion process, evaluating the influence of the inoculum source and their concentration. Thus, three inocula sources were compared: a flocculent sludge from an anaerobic digester treating the sewage sludge of a municipal wastewater treatment plant (MWTP) and two granular anaerobic sludges from a mesophilic upflow anaerobic sludge blanket (UASB) reactor treating effluents from sugar beets and from a mesophilic internal circulation reactor treating brewery

wastewater. Two inoculum concentrations (IC) (10 and 25 g COD/L) were tested for each inoculum, keeping constant the ISR at 2 (on a COD basis).

4.2.2. Materials and methods

HTC process

HTC was performed at 208 ºC in a 4 L ZipperClave® pressure vessel electrically heated using 1.5 kg of DWAS (85% moisture) which was collected from a full-scale membrane bioreactor treating industrial wastewaters from a cosmetics factory. The operating temperature was reached at a heating rate of 3 ºC/min and maintained for 1 h. The reaction was stopped by cooling with an internal heat exchanger using tap water. The slurry obtained (470 g of wet hydrochar and 530 g of LF for each kg of wet material treated) was centrifuged (1400 g for 1 h) by a SIGMA 3-16L centrifuge equipped with a fixed angle rotor (cod. 12159). The liquid fraction was recovered by filtration (0.45 µm) and was maintained at 4 ºC to be used as substrate of the anaerobic digestion tests performed.

Substrate and inocula seed for anaerobic experiments

The main characteristics and composition of the LF were as follows (given as average values of three determinations with standard deviations): pH: 5.1±0.1; soluble COD (SCOD): 95.5±0.4 g/L; biochemical oxygen demand (BOD_5): 25.6±1.1 g/L; total solids (TS): 55.7±0.5 g/L, volatile solids (VS): 46.2±0.5 g/L; total organic carbon (TOC): 42.6±0.9 g/L; and TKN: 8.7±0.1 g/L. The substrate was analysed by GC/MS and HPLC/RI. These analyses allowed identification of the presence of nitrogen-containing species (pyrazines and aromatic amines) and oxygenated aromatic compounds (phenols and furans) and determination of the VFA concentration, respectively.

Three different inocula, collected from industrial full-scale anaerobic reactors operating under mesophilic conditions (35 ºC), were used for the anaerobic digestion batch experiments:

- Inoculum 1 (BW): Granular inoculum obtained from an internal circulation anaerobic reactor treating brewery wastewater.
- Inoculum 2 (SB): Granular anaerobic sludge from an UASB reactor treating sugar beet effluents.
- Inoculum 3 (MS): Flocculent anaerobic sludge from a sewage sludge digester of a MWTP.

The main characteristics of the three inocula are collected in Table 4.2.1 (average values of three determinations with standard deviations). Substantial differences can be observed due to the substrate treatment and the reactor configuration of the full-scale facilities.

Table 4.2.1. Main characteristics of the seed inocula.

Inoculum source	pH	TS (g/kg)	VS (g/kg)	TCOD (g/L)	TKN (g N/L)
BW	7.6±0.1	61.9±0.9	55.7±0.9	91.2±1.4	2.2±0.1
SB	7.9±0.1	162.4±4.0	37.8±0.6	73.4±0.1	4.4±0.1
MS	7.2±0.1	43.3±0.3	26.5±0.3	43.5±1.2	2.2±0.1

Batch anaerobic experiments

Anaerobic digestion runs were carried out batch-wise in 120 mL glass serum vials, filled with 60 mL of a suspension of inoculum, substrate and a basal medium with macro- and micronutrients, as described elsewhere [29] following the recommendations of Holliger et al. [42]. The reaction medium was previously flushed with N_2 for 3 min in order to achieve anaerobic conditions. Then, the vials were sealed with rubber stoppers and metallic crimps. The vials were maintained in a static incubator at mesophilic temperature (35±1 ºC) and manually mixed on a daily basis. As indicated before, two IC values (10 and 25 g COD/L) were tested with each inoculum. Taking into account the above cited literature and previous studies developed with LF [20], an ISR of 2 (on the basis of COD) was chosen for experiments performing. This ISR corresponds to 2.6 for BW and MS inocula and to 2.2 for SB one on a VS basis. All the experiments were run for approximately 40-45 days until no significant gas production was observed or less than 5% of the total produced (on the last day) [42].

Triplicate blank samples with no substrate were run to determine the background methane from the inocula and triplicate control experiments with starch (Panreac) were also conducted with each inoculum to verify their activity, and yields higher than 85% of theoretical (350 mL CH_4/g COD_{added}) were reached for the three inocula tried. For both IC tested with every inoculum, 9 batch runs were carried out. Six of them were sacrificed every one or two days initially and then weekly to follow the time-course of the anaerobic digestion process. The other three runs were used only for biogas measurements (volume and composition).

Analytical methods

The inocula were characterised by measuring the pH (using a model Crison 20 Basic pH meter), TS and VS according to the standard methods 2540B and 2540E [43]. The

total COD (TCOD) was determined following the method proposed by Raposo et al. [44]. TKN determination has been described elsewhere [20].

The liquid fraction from hydrothermal carbonization, as well as the sacrificed samples (centrifuged and filtered through a 0.45 µm filter), were used to determine the following parameters: pH; partial and total alkalinity (PA and TA) by pH titration to 5.75 and 4.3, respectively [45]; intermediate alkalinity (IA), defined as the difference between TA and PA; SCOD, using the closed digestion and colorimetric standard method 5220D [43]; TOC, measured with an automatic analyser TOC-VCPN (Shimadzu); TKN; and TAN, determined by distillation and titration according to the standard method 4500E [43]. Analyses of individual VFAs (C2-C4) were performed by HPLC/IR (Varian, Agilent Technologies, Santa Clara, CA, USA) [46]. Identification of individual compounds from LF was carried out by GC–MS (CP-3800/Saturn 2200 using a Varian CP-8200 autosampler injector) [15]. The compounds were assessed using the NIST 2008 Library.

Biogas and methane production were measured daily during the first 3 days and eight more times for the rest of the incubation period. Biogas production was determined by a manometric method [47], measuring the pressure increase in each vial by an electronic pressure monitor (ifm, PN 7097). It was expressed at standard temperature and pressure (STP: 273 K, 1 bar). Biogas was subsequently exhausted to re-establish atmospheric pressure. The gas composition (H_2, CO_2 and CH_4) was determined by gas chromatography using a Bruker 450-GC (Goes, The Netherlands) coupled with a thermal conductivity detector (TCD) for H_2 and CO_2 and a flame ionisation detector (FID) for CH_4 [46]. Methane production was calculated by subtracting the amount of methane produced in the blank controls from the methane production of each batch reactor.

Statistical analyses

Methane yields were expressed as mean value±standard deviation (average of three samples). Analysis of variance (ANOVA) was carried out using Origin software (version 9.0). The significant of means values was determined by Fisher's test. Fisher's least significant difference (Fisher's LSD) was calculated at a confidence level of 0.05.

4.2.3. Results and discussion

Fig. 4.2.1 a shows the time-course of the pH during the anaerobic digestion of the LF of dewatered waste activated sludge. The initial pH for all the inocula ranged between 7 and 7.8 and increased during the anaerobic process to 7.5-8.1. As can be seen, this parameter

is more affected for the IC, with higher values for experiments carried out at IC 2.5 and final values varying less than 0.1, than for the type of inoculum. Anyway, these pH values are compatible with the adequate growth of anaerobic microorganisms, including methanogenic *Archaea* [48]. The evolution of alkalinity (Fig. 4.2.1 b) shows a fairly similar trend at each IC value, regardless of the inoculum source. In all cases, the alkalinity increased during the first 8-10 days and then remained almost constant for the rest of the experiment. In the IC 1 runs, alkalinity values of 1900-2100 mg $CaCO_3$/L were reached, while the values for IC 2.5 experiments ranged between 4000 and 5400 mg $CaCO_3$/L. The increase of alkalinity, clearer for IC 2.5 runs, must be due to the release of ammonia nitrogen and carbon dioxide upon the decomposition of the organic matter. This favours the buffer capacity of the system, as has been previously reported [30]. The expected relationship between pH and alkalinity appears clearly.

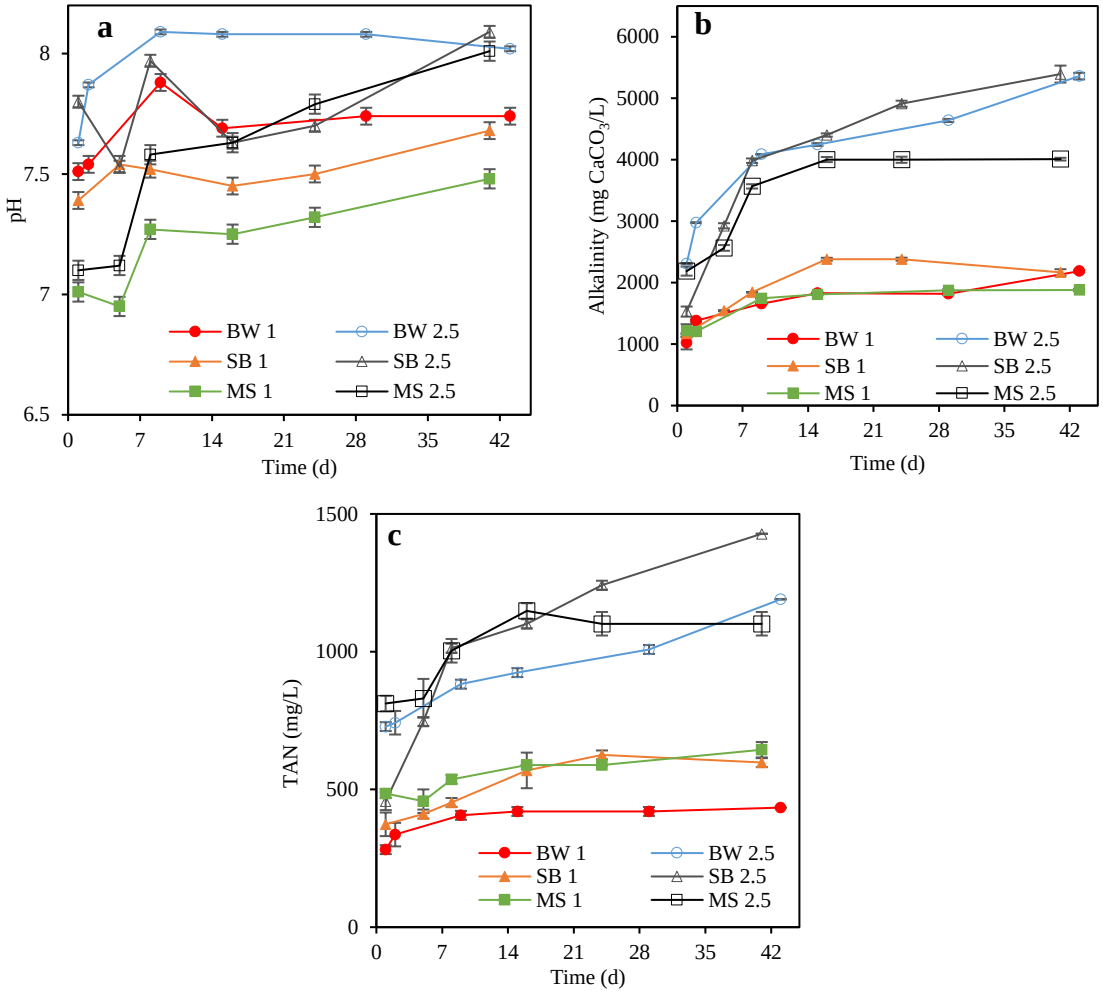

Fig. 4.2.1. Time-course of pH (a), alkalinity (b) and TAN (c) during the anaerobic digestion of the LF of dewatered waste activated sludge.

The evolution of TAN (Fig. 4.2.1 c) showed similar trends with the three inocula as those observed for pH and alkalinity. Percentages above 70% of TAN were released at the 8th day in all the cases, except for SB 2.5 run, which confirm the extent of the hydrolytic stage until that time. Values above 1700 mg N/L could inhibit the biogas yield and promote high VFA concentrations [48], although it was not achieved for any conditions assessed, only SB 2.5 run was close to this value.

The lower initial alkalinity for the experiments with MS inoculum (compared with BW and SB ones) affected the pH of the corresponding runs, especially during the first 5 days (hydrolytic-acidogenic stage). Fig. 4.2.2 shows the time-course of TVFA (4.2.2 a) and SCOD (4.2.2 b), respectively. These parameters provide useful information on the performance of the anaerobic digestion process relative to the acidogenesis level (TVFA evolution) and the degradability of the substrate (SCOD reduction). In the case of TVFA, values in the range of 200-1000 mg COD/L were observed at IC 1 runs during the hydrolytic-acidogenic stage (first 5-8 d), while the final concentration were almost negligible for every experiment. Therefore, no intermediate products in the form of VFA were accumulated. These results are consistent with the trend observed for SCOD removal and with the IA/TA ratios that were maintained within adequate levels, between 0.19 and 0.29. However, certain amounts of SCOD remained at the end of the assays. This fraction of the non-removed COD can be associated with oxygen- and nitrogen-bearing aromatic compounds, generated during the carbonization of the dewatered waste activated sludge and identified in the initial LF [20]. As a representative example, Fig. 4.2.3 depicts the GC/MS chromatograms of the initial and final samples from the SB at IC 1 experiment.

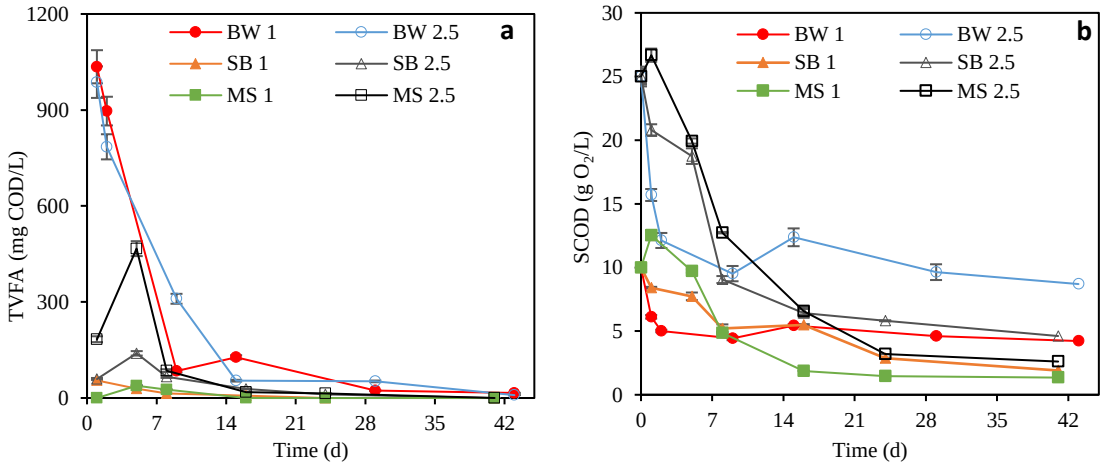

Fig. 4.2.2. Time-course of total volatile fatty acids (a) and soluble chemical oxygen demand (b) during the anaerobic digestion of the LF of dewatered waste activated sludge.

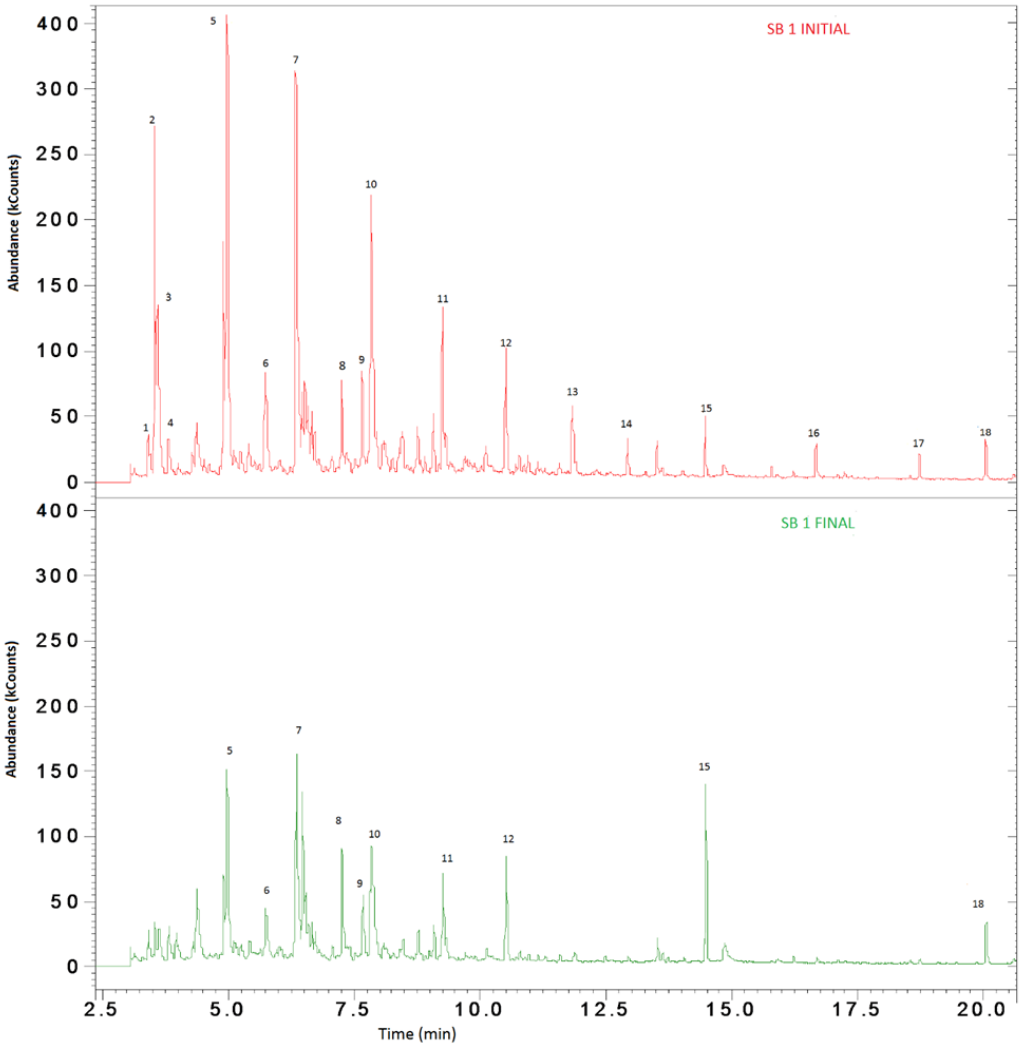

Fig. 4.2.3. GC/MS chromatograms of the initial and final samples of SB at IC 1.

Table 4.2.2 collects the assessed compounds and the corresponding removal percentages in the liquid phase from the IC 1 runs with the three inocula used. Anaerobic digestion led to almost complete removal of the ketone (benzophenone) and aldehyde (4-methoxycinnamaldehyde) species present in the initial samples. Phenols and other oxygenated aromatics were partially removed, but a new phenolic compound (phenol, 2,4-bis(1,1-dimethylethyl)-) appeared as a degradation intermediate. The starting LF showed a high concentration of TKN, probably due to the presence of nitrogen-containing species such as pyrazines and aromatic amines (p-aminotoluene; pyrazine, 2,5-dimethyl; pyrazine, 2-ethyl-5-methyl-; pyrimidine, 4,6-dimethyl-; benzenamine, 3-methyl-; 4,5-dimethyl-ortho-phenylenediamine), which showed different resistances to anaerobic degradation. This fact was more evident in the experiments carried out with BW inoculum, which upheld the highest final SCOD values (Fig. 4.2.2 b), with removal efficiencies between 58 and 65%, while for SB and MS inocula removal efficiencies

ranged between 78 and 90%. The different removal pattern of the organic compounds from the liquid phase could be related to biodegradation and/ or to sorption processes on the sludge, being the latest relevant in the removal of a number of organic compounds (toxicant/ inhibitors) previously to anaerobic biodegradation [49].

Table 4.2.2. Removal/generation of chemical species upon anaerobic digestion of the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge for samples at IC 1 and every inoculum.

Compound	**Retention time (min)**	**Peak number**	**Removal (%)***		
			BW	MS	SB
Aldehydes					
4-Methoxycinnamaldehyde	12.9	14	>99	97	87
Nitrogenated compounds					
p-Aminotoluene	3.4	1	n.d.	0	0
Pyrazine, 2,5-dimethyl	3.5	2	0	23	88
Pyrimidine, 4,6-dimethyl-	3.6	3	0	8	81
Benzenamine, 3-methyl-	3.8	4	3	0	27
Pyrazine, 2-ethyl-5-methyl-	4.9	5	0	32	61
4,5-Dimethyl-ortho-phenylenediamine	6.4	7	0	9	37
Oxygenated aromatics					
4-Isopropylcyclohexanone	5.7	6	n.d	38	78
7H-Dibenzo(a,g)carbazole, 12,13-dihydro-	7.3	8	0	0	0
Benzene, 1,2,4,5-tetramethyl-	7.6	9	0	40	39
Phenol, 2,3,5,6-tetramethyl-	7.8	10	13	42	93
Phenol, 2-methyl-6-(2-propenyl)-	9.2	11	>99	34	44
Benzene, 1-methoxy-4-(1-propenyl)-	10.5	12	20	18	23
Phenol, p-tert-butyl-	11.8	13	85	62	100
Phenol, 2,4-bis(1,1-dimethylethyl)-	14.5	15	gen	gen	Gen
Benzophenone	16.6	16	99	99	87
1,2,3,4,5,6-Hexahydro-1,1,5,5-tetramethyl-2,4a-methanonaphthalen	18.7	17	n.d.	n.d	>99
1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	20.0	18	0	0	13

*with respect to peak area
nd: not detected
gen: generated

Methane yield

Incubation with different inocula resulted in dissimilar methane yields (mL STP CH_4/g COD_{added}), as seen in Fig. 4.2.4. SB and MS achieved the highest methane yields for the IC 1 runs, with 138±18 and 127±13 mL STP CH_4/g COD_{added}, respectively. Meanwhile, with BW, the highest methane yield was obtained for the IC 2.5 run, with 177±5 mL STP CH_4/g COD_{added}. The BW granular sludge gave the highest methane yields. Neves et al. [50] and Rincón et al. [29] reported better results with granular than with flocculent sludge for kitchen wastes and sunflower oil cake, respectively. De Vrieze et al. [51] also recommended the use of granular sludge as inoculum because of its higher methanogenic abundance and diversity, which determines a higher activity compared with other kinds of inocula. The low yield reached with SB granular inoculum could be explained by its poor granulation. In addition, this inoculum has the highest TKN values, releasing the highest concentration of TAN (see Fig. 4.2.1 c), the obtained value ≈1500 mg N/L is close to the considered as inhibitory as has been commented above. Additionally, SB presented the highest concentration of TS but the lowest percentage of VS (23.2%); therefore, the expected activity should be lower. In this way, the methane yield was 9 and 35% higher in the 1 and 2.5 experiments, respectively, with MS and 14 and 79.5% higher with BW. Variation of the IC, which resulted in modifications of substrate concentration at a constant ISR, showed significantly different effects on the methane productivity, depending on the inoculum. Increasing the IC from 10 to 25 g COD/L improved the methane yield by 23% with the BW inoculum but decreased it by 22% with the SB one. However, the IC within the range tested did not affect the methane production rate with the MS inoculum, after an observed lag period. Significant differences of maximum methane yield were found for BW 2.5 run ($p<0.05$), while the differences of this parameter were not significant ($p>0.05$) for SB 1, BW 1, MS 1 and MS 2.5 experiments (Table 4.2.3). According to Table 4.2.3, SB 2.5 showed significantly lower methane yields than the other types of inocula or inoculum concentrations. The percentage of methane in the biogas was related to the inoculum, reaching up to 82, 73 and 62% with BW, MS and SB, respectively.

Wirth et al. [22] obtained similar methane yields to those of the current work with the liquid fraction from HTC of digested sewage sludge operating in continuous feed mode (120-180 mL STP CH_4/g COD_{added}). Meanwhile, Qiao et al. [18] reported 256.7 mL CH_4/g COD with the LF of mixed sewage sludge. The anaerobic digestion of

the LF from HTC of several residues has been studied recently. The ultimate methane yields are affected by the raw residue nature and moisture and the carbonization conditions (temperature and time). Values in the range of 175-300 mL CH_4/g COD have been reached with the LF from HTC of stillage [23], orange pomace [16], chaff [21], and a mixture of polysaccharides, proteins, and lipids representing food waste [52].

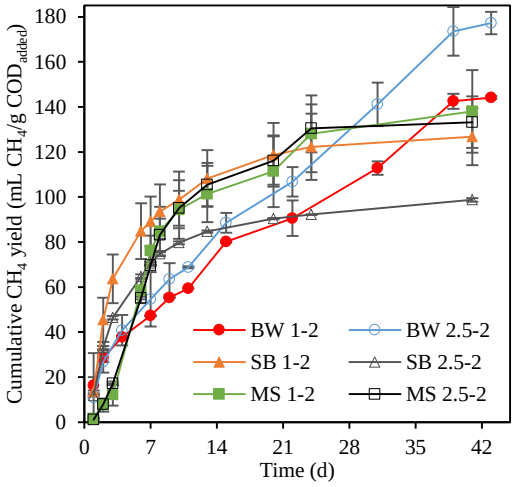

Fig. 4.2.4. Time-course of cumulative methane yield during the anaerobic digestion of the LF of dewatered waste activated sludge.

The results of methane yield from the experiments with the SB and BW inocula were fitted to a first-order kinetic model (Eq. 4.2.1) frequently applied to methane production from anaerobic digestion experiments [24-26, 52-55]. The Gompertz model (Eq. 4.2.2) has been used for the MS experiments due to the initial lag-phase observed with this inoculum [15,25,36,56-58]:

$$G = Gm \cdot [1 - \exp(-k \cdot t)] \qquad \text{Eq. 4.2.1}$$

$$G = Gm \cdot [1 - \exp(-k \cdot (t - \lambda))] \qquad \text{Eq. 4.2.2}$$

where G represents the cumulative methane yield at time t; G_m is the ultimate methane yield of the substrate tested, i.e., the final value when no more gas is released from the reactor; k is the specific rate or apparent kinetic constant; and λ is the extent of the lag-phase (d). Origin software (version 8.0) was used to fit the experimental data to Eq. 4.2.1 and Eq. 4.2.2. Table 4.2.3 summarises the k values with 95% confidence, as well as the corresponding values of Gm and R^2. The high values of the coefficient of

determination R^2 (>0.96) and the low values of the confidence limits of the parameters show the good fit of the experimental data to the proposed models. An initial lag-phase was observed with MS inoculum, which could be related with their flocculent structure. In fact, an initial hydrolysis (cellular lysis) determined by the increase of SCOD was observed only for this inoculum (Fig. 4.2.2 b), showing a very low methane yield until an acclimation period of 5-7 days. Interestingly, after that period, methane rate production with MS inoculum was considerably higher than the obtained with SB and BW inocula. Actually, the highest *k* values were obtained for MS inoculum (≈0.29 d^{-1}) while significantly lowest values were reached for BW (≈0.04 d^{-1}), that reveals a slower digestion.

Table 4.2.3. Values of the apparent kinetic constant (k), lag phase (λ) and fitted (Gm) and experimental (Gm_e) maximum methane yield.

Experiment	**k (d^{-1})**	**λ (d)**	**Gm (mL CH_4/g COD_{added})**	**R^2**	**Gm_e (mL CH_4/g COD_{added})**
SB 1	0.196±0.016	-	121.6±3.3	0.974	$127±13^b$
SB 2.5	0.198±0.012	-	91.0±1.8	0.987	$99±1^c$
BW 1	0.043±0.009	-	165.3±17.2	0.966	$144±1^b$
BW 2.5	0.034±0.006	-	228.4±24.2	0.983	$177±5^a$
MS 1	0.302±0.047	5.19±0.39	124.0±4.9	0.969	$138±8^b$
MS 2.5	0.281±0.027	5.35±0.25	126.4±3.2	0.988	$133±11^b$

Means with different superscript significant differ ($p<0.05$)

4.2.4. Conclusions

The results obtained in this study reveal the importance of the inoculum origin and structure for the treatment of the LF of dewatered waste activated sludge by anaerobic digestion. IC increase can improve the methane yield depending on the inoculum source. High COD removal efficiencies were achieved for each inocula studied and the methane yields were very dependent of the inoculum source. Among the three inocula tested, BW appears to be the best in terms of methane production, although the significantly lowest values of the kinetic constant reveal a slower digestion. Further research will be required to evaluate the co-digestion of this liquid by-product with primary sludge in order to integrate the HTC of waste activated sludge in wastewater treatment plants.

4.2.5. References

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Chapter 5:

The anaerobic co-digestion of the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge with primary sewage sludge

5.1

Anaerobic co-digestion of the aqueous phase from hydrothermally treated waste activated sludge with primary sewage sludge. A kinetic study

J.A. Villamil, A.F. Mohedano, J.J. Rodriguez, M.A. De la Rubia, Anaerobic co-digestion of the aqueous phase from hydrothermally treated waste activated sludge with primary sewage sludge. A kinetic study, J. Environ. Manage. 231 (2019) 726–733

Abstract

The mesophilic anaerobic co-digestion of the liquid fraction (LF) from hydrothermal carbonization (HTC) of dewatered waste activated sludge (DWAS) with primary sewage sludge (PSS) has been studied. Mixtures of different composition (25, 50 and 75% of LF from HTC on a chemical oxygen demand (on a COD basis), as well as the individual substrates, have been tested using two inocula (flocculent (FS) and granular (GS) sludges). Methane production decreased as the LF/PSS ratio increased, which can be related to the presence of recalcitrant compounds in the LF, such as alkenes, phenolics, and other oxygen- and nitrogen-bearing aromatics hard-to-degrade through anaerobic digestion. Methane yield reached 248±11 mL STP CH_4/g COD_{added} with the GS inoculum and 25% LF. A 74 and a 30% increase of methane production was achieved in the 25% LF runs respect to the obtained in the similar experiments with LF as sole substrate, using the FS and GS inocula, respectively. In those late runs, the COD was reduced more than 86%, with a negligible concentration of total volatile fatty acids. With both inocula, total Kjeldahl nitrogen hydrolysis increased as the LF to PSS mixture ratio decreased, reaching values higher than 79% at the end of the experiments. Methane yield values fitted well the first-order, Cone and Weibull kinetic models for both inocula. Significant differences in the kinetic constant values, ranging from 0.100-0.168 d^{-1} and 0.059-0.068 d^{-1}, were found with the FS and GS inocula, respectively. The results obtained support the potential integration of HTC of DWAS in wastewater treatment plants.

5.1.1. Introduction

The management of sewage sludge (mixed sewage sludge) plays a crucial role in wastewater treatment plants (WWTP). The huge generation of this biowaste could reach 13 Mt/year (on a dry basis) in 2020 in the European Union [1]. Moreover, the high costs associated with sewage sludge treatment accounts for an essential part of total operational costs [2]. The conventional treatment of sewage sludge in large WWTP is mainly performed by anaerobic digestion. This technology allows recovering energy as biogas (≈36 MJ/Nm^3) in combined heat and power systems (cogeneration) and generators, to produce electricity and heat [3-5]. However, anaerobic digestion suffers from some drawbacks such as the negative effect of biodegradable carbon and nutrient imbalance of the substrate on the biogas production. Optima carbon-to-nitrogen ratios (C/N) between 20 and 30 are commonly accepted for adequate anaerobic digestion. In this sense, sewage sludge is characterized by a high organic matter content (60-70% on a dry basis), a

relatively low C/N ratio, ranging between 6 and 16, and high buffer capacity, which affects to the nutrition balance of microorganisms [6]. Therefore, the anaerobic co-digestion (AcoD) of sewage sludge with carbon-rich substrates with an adequate C/N ratio has been widely used for nutrients adjustment. These include the organic fraction of municipal solid wastes (OFMSW), food wastes, livestock and poultry manure and microalgae, among others [7-11].

There are other technical solutions available for sewage sludge management such as incineration, composting and landfilling [12-14]. However, the emissions of greenhouse gases during incineration or the odor caused by composting process, make these solutions less attractive in many cases [15]. Several thermal processes for energy recovery, such as pyrolysis or gasification, are gaining attention, since the resultants products may be used as bio-fuels or source of chemicals [16-17]. The main drawback of these technologies is the high energy requirements needed for moisture reduction.

In this context, hydrothermal carbonization (HTC) can be an environmentally friendly technology to manage sewage sludge allowing to reduce the energy-intensive drying of high-moisture organic feedstocks, as well as to produce the so-called hydrochar, a valuable solid fuel [18]. In this thermochemical process, wet biomass is treated within the range of 180 to 250 ºC and the corresponding equilibrium pressure [19,20]. Different reactions such as hydrolysis, dehydration, decarboxylation, condensation, and polymerization occur, yielding the abovementioned hydrochar, a gas stream (mainly CO_2) and a liquid fraction (LF from HTC) containing volatile fatty acids (VFAs), furan compounds, glucose, phenols, pyrazines, pyrroles, among others [21-23]. Hydrochar from sewage sludge can be used as fuel due to its good higher heating value ((HHV) ≈ 19- 24 MJ/kg), comparable to sub-bituminous coals [21]. Moreover, this carbon material can be applied in soil amendment, environmental remediation and as low-cost adsorbent [24,25]. The liquid by-product from dewatered waste activated sludge (DWAS) carbonization is characterized by high organic matter and nitrogen contents [23,26,27] and must be treated to avoid adverse environmental impacts. Taking into account the presence of several compounds readily biodegradable (formic, acetic, iso-butyric and butyric acids), this fraction can be valorized as a substrate for anaerobic digestion [28-30]. The main drawback for that is its low C/N ratio (around 7) [22]. Thus, AcoD with PSS can provide a potential solution which would allow the integration of waste activated sludge HTC in the scheme of sludge processing in WWTP with the

benefit of producing hydrochar in addition to biogas. Fig. 5.1.1 shows a proposal of a flow diagram for this approach. Firstly, the WAS is thickened and then dewatered (1), reaching a dry solids concentration from 15 to 35%. Immediately afterward, the dewatered WAS (DWAS, 2) is carbonized obtaining a slurry (liquid and solid fraction) which is dewatered (3). This solid fraction (wet hydrochar) can reach a solids concentration around 50-80% [31-33]. A value of 0.13 g volatile solid (VS) of LF/g VS of DWAS can be obtained from the liquid fraction from HTC, while PSS varies in the range 0.6-1.0 g VS of DWAS /g VS of PSS. Subsequently, the LF and PSS are mixed (4), reaching a ratio of 0.08-0.13 g VS of LF/g VS of PSS and 0.04-0.25 g COD LF/g COD mixture (4-25% COD of LF). After that, The PSS and LF are co-digested (5), and the methane produced could be used as fuel in a generation or cogeneration power plant (6). Finally, the wet hydrochar must be dried (7) to be used as a solid fuel in a combustion process (8).

The aim of the current work is to evaluate this new concept for sewage sludge management. Mesophilic anaerobic co-digestion of mixtures of the LF from HTC of dewatered waste activated sludge and thickened primary sewage sludge, as well as the two bare substrates (PSS and LF), have been tested using two fairly different inocula (a flocculent sludge from a mesophilic digester of a municipal wastewater treatment and a granular ones from a brewery wastewater treatment plant). Several key parameters (alkalinity, Total Kjeldahl nitrogen (TKN), total ammoniacal nitrogen (TAN), VFA, COD and methane yield) of anaerobic process were assessed upon digestion time. Finally, cumulate methane production was fitted to widely applied kinetic models (first order, Gompertz, modified Gompertz, Cone, and Weibull equations) in anaerobic digestion.

Waste activated sludge (WAS) was selected for HTC experiments instead of a mixture of both primary (PSS) and WAS, because of some advantages: (i) Improve the quality of the hydrochar since WAS has lower ash content (usually around 20%) versus more than 30% of PSS and (ii) increase of the potential phosphorus recovery from the liquid fraction since waste activated sludge presents higher P content [34,35]. In addition, it is well known that waste activated sludge shows poor digestibility compared to PSS.

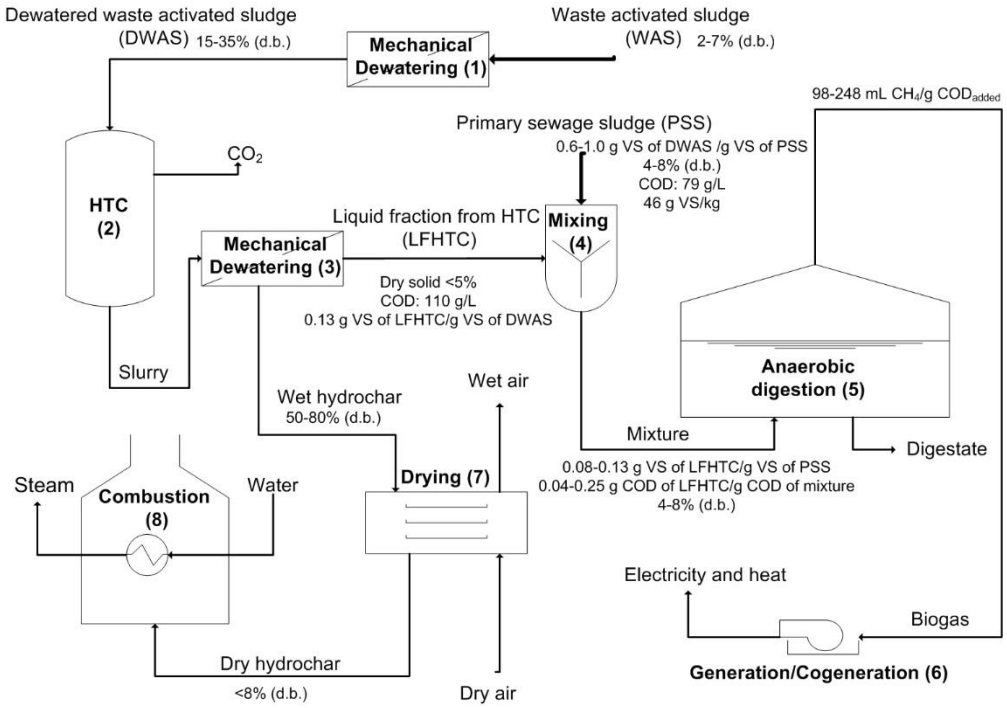

Fig. 5.1.1. Integration of HTC of dewatered waste activated sludge in a WWTP.

5.1.2. Materials and methods

Inocula and substrates characterization

Two different inocula were used: (i) An anaerobic flocculent sludge (FS inoculum) from a full-scale mesophilic digester treating mixed sewage sludge, and (ii) a granular inoculum obtained from a high rate anaerobic reactor, which treats brewery wastewater (GS inoculum). Table 5.1.1 depicts representative analysis of those inocula.

Table 5.1.1. Representative analysis[a] of the inocula (FS and GS) and substrates (PSS and LF).

	Inoculum		**Substrate**	
	FS	**GS**	**PSS**	**LF**
pH	6.9±0.1	7.2±0.2	5.1±0.1	4.9±0.2
TS (g/kg)	21.1±0.1	46.1±0.7	53.1±0.1	51.9±0.5
VS (g/kg)	13.9±0.3	40.3±0.1	45.7±0.1	24.0±0.5
TCOD (g O_2/L)	24.8±0.8	91.2±1.4	78.9±4.2	110.1±2.3
TKN (g N/L)	3.9±0.2	5.1±0.1	3.8±0.3	8.4±0.6
Na (mg/g)	3.0±0.1	0.8±0.1	3.1±0.1	1074.0±11.6[b]
Mg (mg/g)	3.7±0.1	0.1±0.0	3.8±0.2	23.2±1.3[b]
Al (mg/g)	8.9±0.1	0.6±0.0	9.5±0.4	15.8±0.7[b]
K (mg/g)	4.7±0.1	0.5±0.1	4.9±0.8	1182.7±66.1[b]
Ca (mg/g)	39.2±1.4	0.3±0.1	33.0±0.3	67.5±4.4[b]
Fe (mg/g)	24.8±0.5	<0.1	28.5±0.5	32.5±0.1[b]

[a] Average values of three determinations with standard deviations.
[b] (mg/L)

LF was obtained from HTC of DWAS (15% dry matter) was collected from a cosmetic factory full-scale membrane bioreactor (Madrid, Spain), frozen (-20 ºC) and stored before use. HTC experiments were conducted in a 4 L stainless steel reactor (ZipperClave). In each batch experiment, approximately 1.5 kg of the DWAS was loaded into the vessel. The chosen temperature (208 ºC) was reached heating at 3 ºC/min and maintaining the carbonization time for 1 h. Once cooled, the liquid fraction was centrifuged and filtered (0.45 µm). Table 5.1.2 reports a representative analysis of the DWAS and the resulting hydrochar. PSS was drawn from the thickener of a WWTP (Madrid, Spain). Table 5.1.1 includes representative analysis of both substrates (PSS and LF).

Table 5.1.2. Representative analysis[a] of the dewatered waste activated sludge and the resulting hydrochar (% wt., d.b.).

	Waste activated sludge	**Hydrochar**
C (%)	41.5±0.1	43.1±0.2
H (%)	6.0±0.1	5.8±0.1
N (%)	6.8±0.2	4.6±0.1
S (%)	0.7±0.1	0.2±0.1
O[b] (%)	31.3±0.2	26.5±0.1
Ash content (%)	13.7±0.1	19.7±0.2
Volatile matter (%)	73.6±0.1	65.4±0.3
Fixed carbon[c] (%)	12.7±0.1	14.9±0.2
HHV (MJ/kg)	17.6±0.1	21.6±0.1

[a] Average values of three determinations with standard deviations.
[b] By difference
[c] 100 – (moisture + ash + volatile matter).

Batch anaerobic experiments

AcoD experiments were performed in 120 mL glass digesters. Each flask contained a final concentration of 10 g COD/L inoculum, and different concentrations of PSS and LF, together with a stock mineral medium solution and deionized water to make up the working volume (60 mL), following the indications provided by Holliger et al. [36]. Blank tests were performed with inoculum and mineral medium. Tests with starch as sole substrate were also carried out as positive controls. The vials were flushed with N_2 to get anaerobic conditions and placed in a shaking water bath at 35±1 ºC. An ISR of 2 on a COD basis (or 1.7 on a volatile solid (VS) basis) were selected as operational conditions. All the experiments were run until the accumulated gas production remained essentially unchanged, so that biodegradation could be considered essentially completed. Mixtures of different LF to PSS ratios (on a COD basis) (25%, 50% and 75% LF), as well as the two bare substrates (LF and PSS) were tested. These co-substrates are referred as 0% LF,

25% LF, 50% LF, 75% LF, and 100% LF. Nine glass reactors were used for each LF to PSS ratio (0% LF, 25% LF, 50% LF, 75% LF, and 100% LF), sacrificing six of them for the analysis of the typical anaerobic digestion variables (alkalinity, total Kjeldahl nitrogen (TKN), total ammoniacal nitrogen (TAN), VFA and COD) and the other three were used only for biogas characterization (volume and composition). These three reactors were not opened at any time and the volume of digested mass did not change. Moreover, three blank tests with only inoculum and three positive control tests with starch as the sole substrate were performed with each inoculum. Therefore, 102 vials were arranged for the two inocula used.

Analytical methods

Elemental composition (C, H, N, S) content of DWAS and hydrochar was determined using a LECO CHNS-932 Elemental Analyzer. ASTM methods D3173-11, D3174-11 and D3175-11, were used to determine the moisture, ash and volatile matter, respectively. Total solids (TS), VS, soluble COD (SCOD) and TAN, were measured using standard methods (2540b, 2540d, 5220-d and 4500-NH_3[37], respectively). pH was measured with a Crison Basic pH meter. Alkalinity was measured by titration with 0.02 N H_2SO_4 to endpoints of pH 5.75 and 4.3, allowing calculation of total (TA), partial (PA) and intermediate alkalinity (IA) [38]. Total COD (TCOD) was determined by the proposed method by Raposo et al. [39]. TKN was determined as it has been described elsewhere [22], total organic carbon (TOC) was measured with TOC-VCPN (Shimadzu) automatic analyzer. Volatile fatty acids (VFA) were quantified in a Varian 430-GC gas chromatograph [40]. Chemical species were identified in a GC–MS CP-3800/Saturn 2200 using a Varian CP-8200 autosampler injector [40].

Biogas volume produced was measured by an electronic manometer (ifm, PN 7097) and expressed at standard pressure and temperature conditions (STP) (273 K, 1 bar). Gas composition (H_2, H_2S, CO_2 and CH_4) was analyzed by a Thermo Scientific Trace 1310 gas chromatography [40]. Cumulative methane yield on the last day for FS and GS inocula, were assessed by analysis of variance (ANOVA) using Origin software (version 9.0). Fisher's least significant difference (Fisher's LSD) was calculated at a confidence level of 0.05.

5.1.3. Results and discussion

Fig. 5.1.2 shows the TKN values and the evolution of TAN upon the AcoD of the two substrates tested. As can be seen, the hydrolytic stage was shorter for the experiments

with the FS inoculum (Fig. 5.1.2 a) than for those with GS (Fig. 5.1.2 b). TKN hydrolysis decreased at increasing the HTC percentage in the mixture, reaching similar final values (79-95%) for each mixture ratio with both inocula. Final TAN values were within the range of 600-800 and 460-650 mg N/L for the experiments with FS and GS, respectively, much lower than the considered inhibitory value for methanogenic microorganism (1700 mg N/L) [41]. The pH values (6.8-7.3) remained relatively constant in all the runs within the adequate range for methanogenic Archaea growing [42].

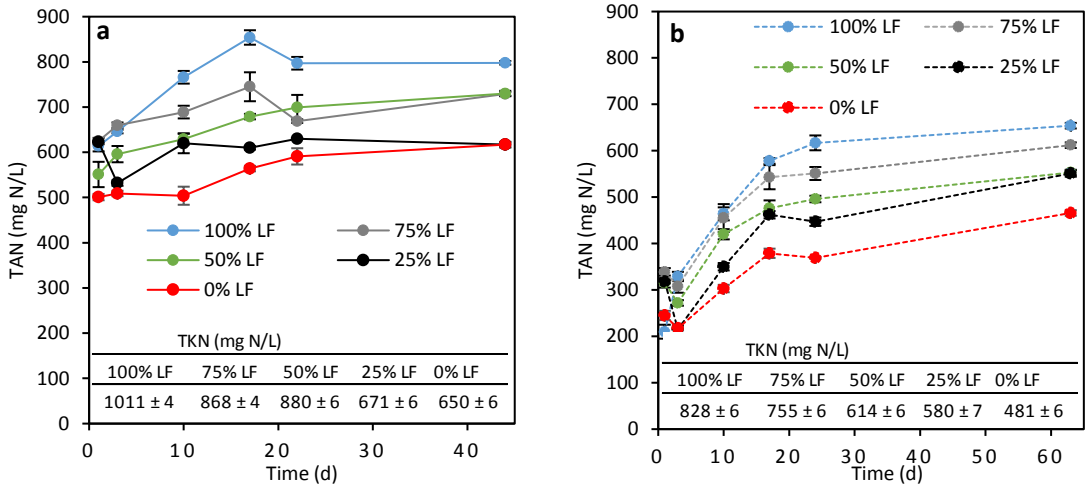

Fig. 5.1.2. Time-course of total ammonia nitrogen (TAN) along the anaerobic co-digestion of PSS and LF with FS (a) and GS (b) inocula. Tables show the TKN values.

Fig. 5.1.3 shows the evolution of alkalinity along the experiments. The initial TA ranged from 1.1 to 1.6 g/L $CaCO_3$ and showed a continuous increase along the anaerobic process, probably due to the release of carbon dioxide and ammonia nitrogen upon the decomposition of the organic matter with time, which improves the buffer capacity [43]. Final TA values in the range of 2.4-2.8 g/L $CaCO_3$ were reached, providing enough buffer capacity (>2 g/L $CaCO_3$) as has been recommended in the literature [44,45].

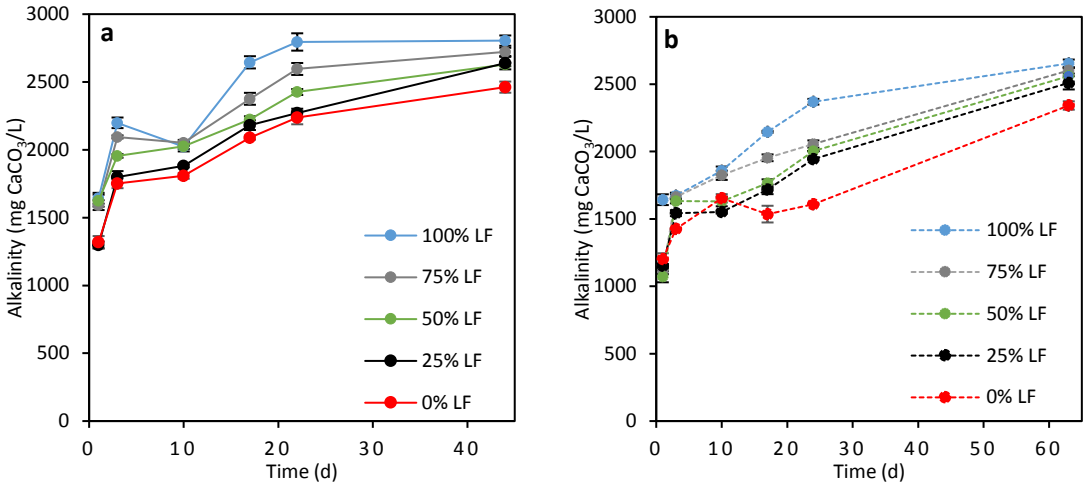

Fig. 5.1.3. Time-course of total alkalinity along the anaerobic co-digestion of PSS and LF with FS (a) and GS (b) inocula.

Fig. 5.1.4 depicts the time-course of total VFA (TVFA) expressed as mg COD/L. The concentration of acetic, propionic and iso-valeric acids in the LF of DWAS, yielded values of 3532±123 mg/L, 620±10 mg/L and 78±19 mg/L, respectively. In the FS experiments (Fig. 5.1.4 a), values of COD attributable to VFA ranged from 455 to 805 mg COD/L in the first days, being around 50-60% acetic acid, the principal substrate of methanogens. TVFA concentration decreased after the hydrolytic-acidogenic stage, reaching negligible values after 10 days digestion time. The TVFA concentrations in the GS experiments (Fig. 5.1.4 b) were significantly higher than the obtained with FS along the first days, reaching values between 778 and 1284 mg COD/L, mainly acetic (60-82%) and propionic (39-16%) acids. In this case, some remaining TVFA (acetic acid) were detected until day 30. Therefore, no VFA were accumulated under the experimental conditions tested, which means that there was no imbalance in the anaerobic process with none of the inocula used.

Fig. 5.1.5 shows the evolution of SCOD upon digestion time. The initial SCOD values in all the experiments were around 5 g COD/L. Somewhat higher COD removal was achieved with the granular inoculum (78-95% vs. 70-87%). Similar SCOD removal (80%) for anaerobic batch reactor treating the LF from HTC of digestate (220 ºC-30 min) has been reported [46]. The COD attributable to VFA was less than 27% in the FS runs during the hydrolytic-acidogenic stage. In the GS experiments, the VFAs were consumed completely during that stage (first 10 days). The remaining COD corresponds to refractory compounds which were detected in the LF from HTC of DWAS such as heterocyclic organic species (pyrroles, pyridines), ketones and alcohols [22,23],

inhibiting methanogenesis, mainly in the case of aromatics [47]. It can also be ascribable to pyrazine compounds which are Maillard products generated in HTC reactions between reducing sugars and amino acids [48]. Moreover, the presence of several nitrogen-containing aromatic compounds could be related to the high TKN concentration in the liquid phase.

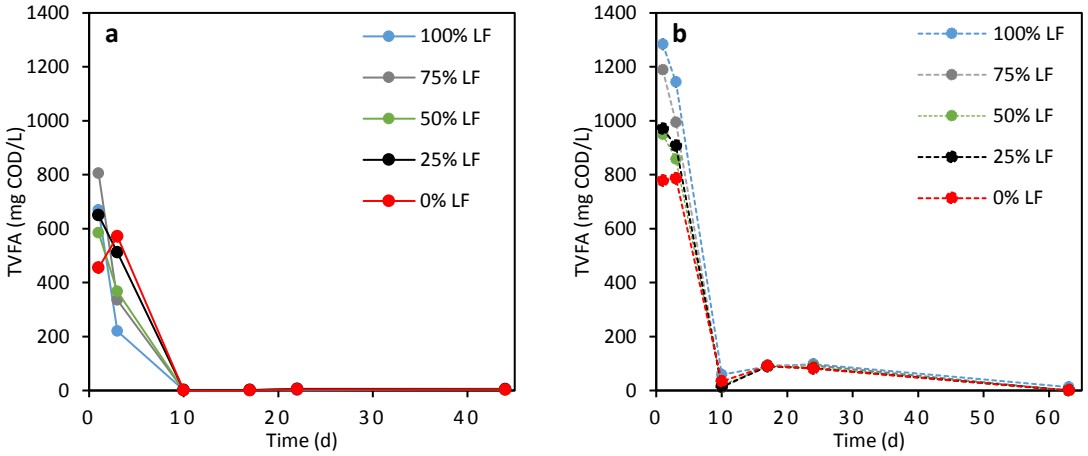

Fig. 5.1.4. Time-course of total VFA along the anaerobic co-digestion of PSS and LF with FS (a) and GS (b) inocula.

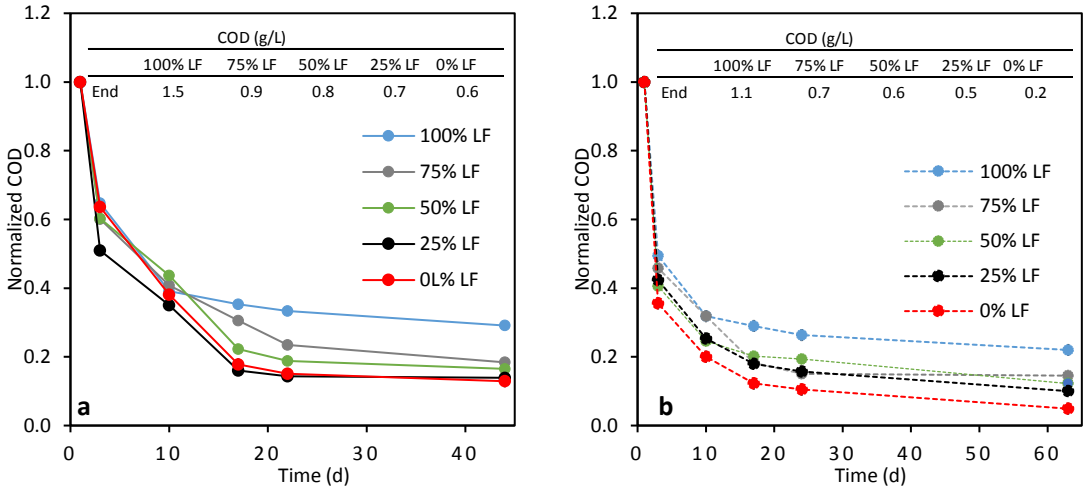

Fig. 5.1.5. Time-course of soluble COD along the anaerobic co-digestion of PSS and LF with FS (a) and GS (b) inocula.

Fig. 5.1.6 shows the cumulative methane production along the anaerobic digestion experiments. Final values ranged within 98±3-204±1 and 191±1-308±1 mL STP CH_4/g COD_{added} for FS and GS experiments, respectively. Several authors have also observed higher methane yields with granular inocula than with the flocculent ones due to the abundance and diversity of methanogenic microorganisms in

the granules [40,49-51]. With both inocula, the methane production increased at decreasing the LF to PSS ratio mixture. In this way, for FS inoculum, a 1.30-fold increase in methane yield was achieved for 25% LF experiment compared to the experiment performed with LF as mono-substrate (100% LF), while for GS a 1.74-fold increase was reached.

The yield obtained with the FS inoculum in the 25% LF experiment (172±1 mL STP CH_4/g COD_{added}) was similar to the reported by Wirth et al. [52] (120-180 mL STP CH_4/g COD_{added}) for the continuous anaerobic digestion of LF from HTC of digested sewage sludge. Qiao et al. [30] reported a methane yield of 257 mL CH_4/g COD operating a continuous UASB reactor, while Aragón-Briceño et al. [46] found values up to 277 mL STP CH_4/g COD_{added} for batch operation, both of them fed with LF from HTC of digested sewage sludge. This yield is similar to the obtained in the current work from the 25% LF mixture with GS inoculum (248±11 mL STP CH_4/g COD_{added}). Recently, De la Rubia et al. [23] have studied the mesophilic co-digestion of the LF from HTC of dewatered waste activated sludge and OFMSW using a flocculent inoculum, reaching an ultimate methane yield within the range of 124±9 and 194±1 mL STP CH_4/g COD_{added}, very close to the obtained now with the FS inoculum. Several studies can be found in the literature dealing with anaerobic digestion of the LF from HTC of several biomass wastes. The ultimate methane yield depends on nature of the raw residue and the HTC conditions (time and temperature). Close values to the obtained in the 25% LF experiments of this study (175-300 mL CH_4/g COD) have been reported with the LF from HTC of lignocellulosic residues [53-55].

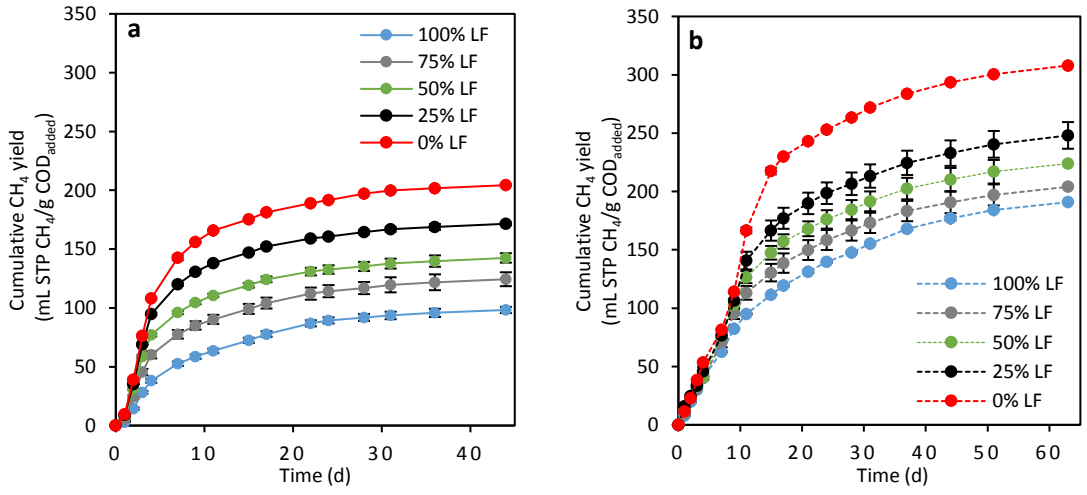

Fig. 5.1.6. Cumulative methane yield along the anaerobic co-digestion of PSS and LF with FS (a) and GS (b) inocula.

Fig. 5.1.7 shows the daily methane production rate, calculated as the derivative of the cumulative methane yield. As can be seen, with the FS inoculum the methane production rate decreased at increasing the relative amount of LF in the mixture. The highest values (12.7-33.3 mL CH_4/g COD·d) were reached in the 2nd day, corresponding with the VFA concentration peak. Lower values (11.1-21.3 mL CH_4/g COD·d) were obtained with the GS inoculum, probably due to mass-transfer limitation of VFA in this granular sludge [56].

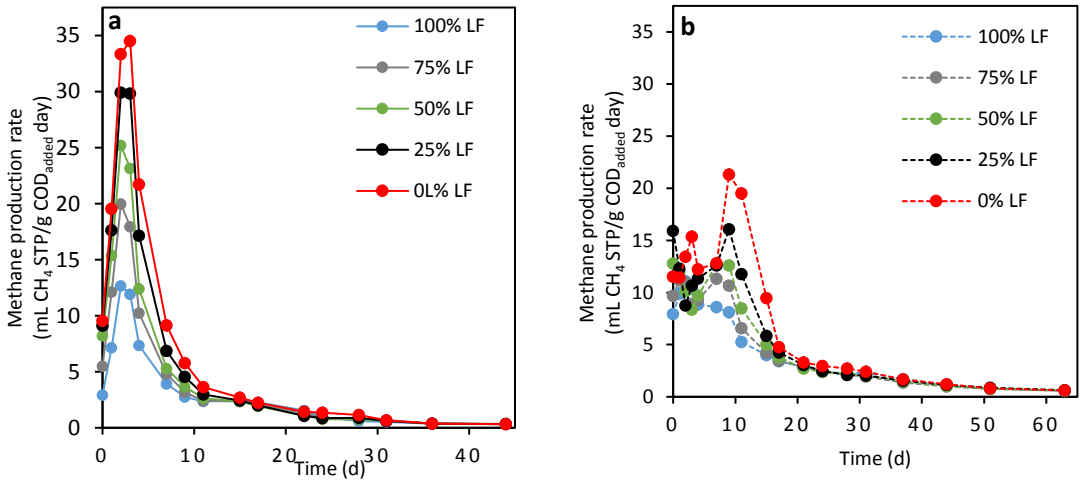

Fig. 5.1.7. Time-course of daily methane production rate along the anaerobic co-digestion of PSS and LF with FS (c) and GS (d) inocula.

The results of methane yield were fitted to first-order, Gompertz, modified Gompertz, Cone and Weibull kinetic models, which have been widely applied for anaerobic digestion [57-61]. Table 5.1.3 collects the above-mentioned kinetic equations. Origin software (version 8.0) was used to fit the experimental data to those kinetic equations. The results are summarized in Table 5.1.4 (FS experiments) and Table 5.1.5 (GS experiments). Except for modified Gompertz model, all the kinetic equation checked describe well the evolution of methane production upon digestion time. In general, the fitting was better for the experiments with the flocculent inoculum (FS). The k values obtained for first-order apparent rate constant fall within the range of 0.100-0.168 d^{-1} and 0.059-0.068 d^{-1} for FS and GS experiments, respectively. The lower k values with the granular sludge can be due to the occurrence of mass-transport limitation [56]. All the k values are higher than the reported by Villamil et al. [22] for the anaerobic digestion of the LF of DWAS (0.031-0.043 d^{-1}) but significantly lower than the previously reported by De la Rubia et al. [23] for the AcoD of the OFMSW with the LF from HTC of waste activated sludge (0.44-0.56 d^{-1}).

Table 5.1.3. Kinetic model checked to fit the experimental results of cumulative methane yield.

Model	Equation	Parameters
First-order	$G(t) = G_{max}[1 - exp\,(-k \cdot t)]$	G (mL CH_4/g COD): cumulative specific methane production G_{max} (mL CH_4/g COD): ultimate methane production k (d^{-1}): specific rate constant t (d): digestion time
Gompertz	$G(t) = G_{max} \cdot exp\,[-exp\,(\mu - \lambda \cdot t)]$	μ (mL CH_4/g COD·d): maximum methane production rate λ (d): lag-phase time constant.
Modified Gompertz	$G(t) = G_{max} \cdot exp\left[-exp\left(\frac{\mu}{G_{max}} \cdot (\lambda - t) \cdot e^1 + 1\right)\right]$	e^1 = 2.7182
Cone	$G(t) = \frac{G_{max}}{1 + (k \cdot t)^{-n}}$	n: dimensionless shape factor
Weibull	$G(t) = G_{max} \cdot [1 - exp\,(-(k \cdot (\lambda - t))^d)]$	d: dimensionless factor

Table 5.1.4. Experimental maximum methane yield* (G_{me}) and fitting parameters for FS experiments.

Model	Parameter	LF to PSS mixture ratio (%)				
		0	**25**	**50**	**75**	**100**
Experimental	G_{me} (mL CH_4/g COD)	204±1[a]	172±1[b]	142±4[c]	124±6[d]	98±3[e]
First-order	G_m (mL CH_4/g COD)	199±4	166±3	137±3	120±2	98±2
	k (d^{-1})	0.160±0.011	0.168±0.012	0.162±0.011	0.137±0.009	0.100±0.006
	R^2	0.985	0.984	0.985	0.986	0.992
	RCS	74.7	54.1	35.2	24.2	9.3
Gompertz	G_m (mL CH_4/g COD)	192±4	161±4	133±3	117±3	100±4
	μ (mL CH_4/g COD·d)	0.987±0.156	0.935±0.165	0.811±0.160	0.757±0.145	0.737±0.116
	λ (d)	0.315±0.043	0.315±0.047	0.271±0.042	0.215±0.032	0.141±0.020
	R^2	0.968	0.962	0.955	0.956	0.960
	RCS	125.0	100.6	78.9	61.6	38.9
Modified Gompertz	G_m (mL CH_4/g COD)	71±2	59±1	50±1	50±3	50±10
	μ (mL CH_4/g COD·d)	8.181±1.032	6.860±0.948	4.616±0.656	2.110±0.399	1.045±0.226
	λ (d)	3.138±0.271	2.965±0.289	3.074±0.371	4.458±1.027	8.916±4.338
	R^2	0.968	0.962	0.953	0.893	0.835
	RCS	125.0	100.6	81.7	149.6	159.6
Cone	G_m (mL CH_4/g COD)	204±3	171±3	144±4	131±4	111±5
	k (d^{-1})	0.236±0.010	0.246±0.012	0.232±0.014	0.185±0.014	0.123±0.012
	n	1.646±0.107	1.591±0.118	1.430±0.116	1.293±0.107	1.208±0.091
	R^2	0.995	0.993	0.992	0.992	0.994
	RCS	27.1	23.9	18.9	14.4	7.1
Weibull	G_m (mL CH_4/g COD)	201±3	169±3	143±3	128±4	106±4
	k (d^{-1})	0.926±0.091	0.925±0.082	0.929±0.067	0.946±0.055	0.938±0.076
	λ (d)	0.807±0.061	0.761±0.061	0.695±0.053	0.677±0.044	0.735±0.043
	d	0.200±0.013	0.206±0.015	0.185±0.016	0.139±0.013	0.095±0.009
	R^2	0.992	0.991	0.992	0.995	0.996
	RCS	31.2	23.8	13.8	7.6	3.7

RCS: Reduced Chi-Square.

*Average values of three determinations with standard deviations. Means with different superscript significant differ ($p<0.05$).

Table 5.1.5. Experimental maximum methane yield* (G_{me}) and fitting parameters for GS experiments.

Model	Parameter	LF to PSS mixture ratio (%)				
		0	**25**	**50**	**75**	**100**
Experimental	G_{me} (mL CH_4/g COD)	308±1[a]	248±11[b]	224±11[b,c]	204±9[c,d]	191±1[d]
First-order	G_m (mL CH_4/g COD)	328±18	249±8	221±6	199±4	186±3
	k (d^{-1})	0.059±0.007	0.066±0.005	0.068±0.004	0.068±0.003	0.060±0.002
	R^2	0.979	0.990	0.994	0.996	0.998
	RCS	251.2	68.2	34.5	17.4	7.7
Gompertz	G_m (mL CH_4/g COD)	292±5	232±4	209±4	191±4	181±5
	μ (mL CH_4/g COD·d)	1.179±0.084	1.007±0.078	0.947±0.083	0.897±0.084	0.820±0.078
	λ (d)	0.147±0.010	0.135±0.010	0.130±0.011	0.122±0.011	0.098±0.009
	R^2	0.990	0.988	0.985	0.983	0.981
	RCS	110.6	78.6	78.8	73.0	68.3
Modified Gompertz	G_m (mL CH_4/g COD)	107±2	85±2	77±2	70±2	67±2
	μ (mL CH_4/g COD·d)	5.804±0.345	4.235±0.266	3.676±0.257	3.149±0.233	2.415±0.18
	λ (d)	8.016±0.327	7.471±0.364	7.291±0.415	7.351±0.462	8.332±0.583
	R^2	0.990	0.988	0.985	0.983	0.981
	RCS	110.6	78.6	78.8	73.0	68.3
Cone	G_m (mL CH_4/g COD)	300±16	264±7	242±5	226±5	235±6
	k (d^{-1})	0.091±0.008	0.090±0.005	0.088±0.004	0.083±0.004	0.060±0.003
	n	1.793±0.249	1.487±0.085	1.382±0.062	1.290±0.047	1.108±0.033
	R^2	0.976	0.995	0.997	0.998	0.999
	RCS	284.1	33.4	16.3	8.7	4.2
Weibull	G_m (mL CH_4/g COD)	297±7	242±6	222±5	205±5	206±5
	k (d^{-1})	0.119±0.949	0.269±0.599	0.514±0.402	0.641±0.273	0.686±0.149
	λ (d)	1.321±0.183	1.1±0.115	0.992±0.083	0.922±0.059	0.833±0.033
	d	0.073±0.006	0.072±0.004	0.071±0.004	0.067±0.004	0.051±0.003
	R^2	0.990	0.992	0.994	0.996	0.999
	RCS	119.8	51.2	30.3	16.2	4.8

*Average values of three determinations with standard deviations. Means with different superscript significant differ ($p<0.05$).
RCS: Reduced Chi-Square

5.1.4. Conclusions

The co-digestion of LF and PSS can provide a feasible way of integrating the HTC of waste activated sludge in a WWTP. Increasing the LF to PSS ratio decreases the methane production, due to the presence of inhibitory nitrogen-containing aromatic compounds detected in the LF. The granular inoculum (GS) was better in terms of ultimate methane yield than the flocculent one (FS). The highest methane yields were found for the experiments with 25% LF (1.76 and 1.30-fold increase with respect to the bare LF, with FS and GS inocula, respectively). With that mixture, SCOD removals around 85-90% were obtained, with no residual VFAs detected. Further research will be required to evaluate the co-digestion of LF and PSS in semi-continuous experiments and with LF below 25% in the mixture.

5.1.5. References

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5.2

Anaerobic co-digestion of primary sewage sludge with the spent liquor from waste activated sludge hydrothermally treated. A new approach for sewage sludge management

J.A. Villamil, A.F. Mohedano, J. San Martin, J.J. Rodriguez, M.A. de la Rubia, Anaerobic co-digestion of primary sewage sludge with the spent liquor from waste activated sludge hydrothermally treated. A new approach for sewage sludge management. Submitted for publication

Abstract

Hydrothermal carbonization (HTC) is a suitable technology for managing waste with a high moisture content such as sewage sludge, providing a coal-like solid product (hydrochar) with an increased heating value and a liquid fraction from HTC (LF) with a high chemical oxygen demand (COD). The aim of this work was to develop a new approach to sewage sludge management involving digestion of primary sewage sludge (PSS) with the liquid fraction from HTC of dewatered waste activated sludge (DWAS). The process was optimized by performing semi-continuous experiments with two different feed mixture compositions (5% and 10% LF, on a COD basis), organic loading rates (OLR; 1.5 and 2.5 g COD/L·d), and temperature regimes (mesophilic and thermophilic). The combination of mesophilic conditions, a 10% LF feed mixture and OLR of 1.5 g COD/L·d provided good results including low concentrations of total volatile fatty acids (TVFA<400 mg COD/L) and ammonium (<1.2 g N/L), in addition to a fairly good methane yield (172±11 mL CH_4/g COD_{added}), 1.15 times the value for the control test with 0% LF. Therefore, HTC applied to DWAS followed by anaerobic digestion of the LF enhanced the valorization of this renewable residue. The proposed global treatment allowed obtaining up to 4.4 times more overall energy produced compared with anaerobic digestion of mixed sludge.

5.2.1. Introduction

The main purpose of wastewater treatment plants (WWTP) is to reduce harmful emissions toward water bodies. Municipal and industrial sewage is most often treated with conventional activated sludge [1]. Despite its high efficiency in removing organic matter, the process produces large amounts of sludge that must be periodically removed. Moreover, treating excess sludge may account for up to 65% of a plant's operating costs [1,2]. New technologies producing less sewage sludge are thus needed.

Primary and secondary sludge from WWTP are usually thickened prior to mixing, stabilized by anaerobic or aerobic digestion and dewatered. Ultimately, sludge is disposed of or valorized by either agricultural usage (composting followed by application to soil), landfilling or thermal treatment [1,2,3]. One of the main hindrances to stabilizing sewage sludge is the low biodegradability of waste activated sludge (WAS) relative to primary sewage sludge (PSS) owing to the rigid structure of the former preventing cell wall disruption and the release of inner cell products, which otherwise facilitate the breakdown of the overall mass. These problems detract from efficiency in stabilizing sewage with biological means [4]. A number of WAS pretreatment technologies including mechanical

(grinding, pressurization, lysis–centrifugation, microwave irradiation, sonication), biological (enzymatic), chemical (alkali or acid pretreatment, ozonation, advanced oxidation processes) and electrical methods have been proposed [5]. Also, sewage sludge can be valorized by using thermal treatments such as conventional heating or steam injection [6,7].

Hydrothermal carbonization (HTC), which is a relatively new process for biomass carbonization, is usually carried out at moderate temperatures (180–250 ºC) and autogenous pressure [8,9]. This process is gaining increasing interest by virtue of its advantages over conventional dry thermal treatments (gasification, pyrolysis, torrefaction, etc.). HTC has some benefits in terms of process performance and economic efficiency, mostly as a result of the ability to process wet feedstock such as dewatered waste activated sludge (DWAS) without the need for prior drying. The streams from HTC comprises a coal-like product called "hydrochar", a liquid phase rich in organic compounds and various gases but mostly CO_2 [10]. Hydrochar can be used as fuel for combustion and gasification, and also as a source of precursors for developing low-cost competitive materials (adsorbents, catalysts, electrodes) upon thermal treatment (pyrolysis, chemical activation, blending) [8]. The liquid fraction from the HTC of DWAS (LF) has high organic matter and nitrogen contents [11]; also, it contains heterocyclic organic compounds (pyrroles, pyridines), phenols, ketones, aldehydes and alcohols, consistent with a common carbonization route [11-13].

Anaerobic digestion is one of the most widely used processes for stabilizing sewage sludge [14]. The widespread use of this technique is a result of its potential advantages, which include a reduction by 30–50% of the volume of sludge ultimately requiring disposal, and the production of energy from methane, which is obtained in excess of the amount required to operate the process [15]. Sewage sludge is usually stabilized under mesophilic or thermophilic conditions (viz., with an optimum temperature of 35 or 55 ºC, respectively) [15]. Thermophilic anaerobic digestion has some advantages over mesophilic digestion including faster reaction and a higher load bearing capacity; as a result, the former exhibits higher productivity and methane production than the latter. However, thermophilic conditions also have some disadvantages such as decreased stability and quality in the effluent; accumulation of NH_3, and volatile fatty acids (VFA); susceptibility to the environmental conditions; and increased net energy requirements relative to mesophilic conditions. Although mesophilic systems exhibit better process

stability and higher microbial richness, they afford lower methane yields and suffer from poor biodegradability [16].

HTC coupled with anaerobic digestion may be an effective and economical choice compared with conventional anaerobic digestion of mixed sludge. The proposed approach letting obtaining a value-added product (hydrochar) with a higher heating value (HHV≈19-24 MJ/kg), comparable to sub-bituminous coals [12], in addition to a liquid by-product containing at least 15% of the initial carbon content [17] and 30% of the total COD [18] and being amenable to anaerobic digestion [10,11,13,19,20]. This technology allows recovering energy as biogas (≈ 36 MJ/Nm^3) in combined heat and power systems (cogeneration) and generators, to produce electricity and heat [21,22]. In this way, the aim of this work was to develop a new approach to sewage sludge management involving HTC of DWAS to obtain hydrochar and then treating the mixture in the liquid stream and PSS by anaerobic digestion. For this purpose, a semi-continuous anaerobic digestion process was optimized in terms of feed mixture ratio (PSS/LF), temperature regime and organic loading rate (OLR). As far as we know, no studies integrating HTC and anaerobic digestion in the sludge line of a WWTP have been carried out. Therefore, a tentative framework for HTC of DWAS as a sound alternative to conventional sewage sludge management is proposed.

5.2.2. Materials and methods

The mesophilic digesters used were seeded with inoculum from a WWTP full-scale mesophilic digester operating in Madrid (Spain). This mesophilic inoculum was adapted at 55 ºC according to Riau et al. [23] for thermophilic experiments. Table 5.2.1 summarizes the properties of the inoculum and the substrates.

Table 5.2.1. Representative analysis of inocula and substrates.

	Inoculum		**Substrates**	
	Mesophilic inoculum	**Thermophilic inoculum**	**PSS**	**LF**
pH	7.5±0.1	8.1±0.1	4.9±0.1	4.8±0.1
Total solids (g/kg)	31.0±1.1	21.0±0.8	31.8±1.4	51.9±0.5
Volatile solids (g/kg)	20.5±0.1	12.5±0.1	26.2±1.3	46.2±0.5
TCOD (g O_2/L)	43.5±1.2	36.6±3.3	61.3±1.8	85.9±1.7
TOC (g/L)	-	-	-	42.6±0.9
TKN (g N/L)	3.9±0.2	4.0±0.3	3.8±0.3	8.7±0.1

PSS was obtained from the primary treatment of the above-mentioned urban WWTP, while HTC of DWAS obtained LF containing 15% dry matter that was previously collected from a full-scale membrane bioreactor in a cosmetic factory also operating in Madrid, Spain. Batchwise HTC runs were conducted in a ZipperClave 4 L stainless steel reactor. In each run, the vessel was loaded with approximately 1.5 kg of DWAS. The target temperature (208 ºC) was reached by heating at 3 ºC/min and carbonization conditions were held for 1 h. The HTC reaction was stopped by a serpentine cooler located insight into the reactor, the liquid fraction was centrifuged (3500 rpm-30 min) and passed through a filter of 0.45 µm pore size. The solid fraction was recovered and dried at 55 ºC for 24 h. Then, the hydrochar was ground and sieved to a particle size in the range of 0.1-0.25 mm. The main characteristics of DWAS and hydrochar are shown in Table 5.2.2.

Table 5.2.2. Representative analysis of the DWAS and the resulting hydrochar[a].

	DWAS	**Hydrochar**
C (%)	48.1±0.1	53.7±0.2
H (%)	7.0±0.1	7.2±0.1
N (%)	7.9±0.1	5.7±0.1
S (%)	0.8±0.1	0.2±0.1
O[b] (%)	22.5±0.1	13.5±0.1
Moisture (%)	5.4±0.1	10.5±0.1
Ash content (%)	13.7±0.1	19.7±0.1
Volatile matter (%)	73.6±0.1	65.4±0.3
Fixed carbon[c] (%)	7.3±0.1	4.4±0.1
HHV (MJ/kg)	17.6±0.1	21.6±0.1

[a]db=dry basis
[b]By difference.
[c]100–(moisture+ash+volatile matter).

Experimental procedure

Tests were performed in thoroughly mixed borosilicate glass digesters each having a total volume of 2.8 L and a working volume of 2 L. The temperature for mesophilic (35 ºC) and thermophilic (55 ºC) conditions was adjusted by recirculating water through the double wall of the reactors. Heat losses were prevented by using insulating coats which also reduced the amount of daylight reaching the reactors. Continuous stirring in the reactors was provided by direct drive stirrers furnished with holed paddles.

The reactors were operated in a semi-continuous mode (one feed per day) at two different PSS to LF mixture ratios (5 and 10% LF on a chemical oxygen demand, COD, basis) for 250 d. A control treatment with PSS as bare substrate was also performed in parallel. Two

different OLRs (1.5 and 2.5 g COD/L·d, corresponding to a hydraulic retention time, HRT, of 44 and 26 d, respectively, under mesophilic and thermophilic conditions) were used. Based on the low volatile solid (VS) concentration provided by LF, an OLR on a VS basis of ca. 3 g VS/L·d was used in all tests. In what follows, the mixtures are referred to as 10% LF, 5% LF and control (PSS), respectively. PSS to LF mixture ratios were chosen according to the results of the batchwise anaerobic digestion of PSS and LF, where inhibition was substantial with LF proportions exceeding 25% in the mixture [24]. Attainment of the steady-state under each set of conditions tested was verified after a period equivalent to 3 times HRT by checking the effluents for constancy in their properties. Samples for characterization were withdrawn during each steady-state period. The effluents from the reactors (raw samples) were centrifuged at 8000 rpm for 15 min and vacuum-filtered through glass microfiber filters of 0.45 μm pore size (soluble samples).

Analytical methods

Total solids (TS), volatile solids (VS), soluble COD (SCOD) and total ammonia nitrogen (TAN) were determined by using standard methods [25] (2540b, 2540d, 5220-d and 4500-NH_3, respectively), while free ammonia nitrogen (FAN) was calculated according to Hansen et al. [26]. pH was measured with a glass electrode (Crison Basic pH meter). Alkalinity was determined by titration with 0.02 N H_2SO_4 to endpoints of pH 5.75 and 4.30, which allowed total (TA), partial (PA) and intermediate alkalinity (IA) to be calculated [27]. Total COD (TCOD) was determined according to Raposo et al. [28] and total Kjeldahl nitrogen (TKN) according to Villamil et al. [11]. Total organic carbon (TOC) was measured with a Shimadzu TOC-VCPN autoanalyzer and volatile fatty acids (VFAs) were quantified on a Varian 430-GC gas chromatograph [29]. Chemical species were identified on a GC–MS CP-3800/Saturn 2200 instrument equipped with a Varian CP-8200 autosampler injector [29]. Biogas volumes were directly measured with a Ritter MilliGas counter (MGC-1 V3.4 PMMA) from Ritter Apparatebau GmbH and collected in Tedlar® gas sampling bags. Gas composition was determined with a Thermo Scientific Trace 1310 gas chromatograph [29].

The elemental composition (C, H, N, and S) of dewatered waste activated sludge and the hydrochar was determined by a CHNS analyzer (LECO CHNS-932). ASTM methods in the analysis sample of coal and coke D3173-11, D3174-12, and D3175-17 were used to determine the moisture, ash and volatile matter, respectively [30]. The metal content was

determined by inductively coupled plasma atomic emission spectroscopy (ICP-MS) using a model Elan 6000 Sciex Perkin Elmer apparatus.

Data analysis and energy yield of DWAS hydrothermally treated

The HHV was determined according to the technical specification UNE-EN 15400 for solid recovered fuels [31] using a calorimetric bomb (IKA C2000). The hydrochar yield (Y_{hyd}), energy densification (E_{dens}), energy yield (E_{yield}), and carbon recovery ($H_{c,recov}$) were calculated as follows:

$$Y_{hyd}(\%) = \frac{mass\ of\ dry\ hydrochar}{mass\ of\ DWAS} \cdot 100 \qquad \text{Eq. 5.2.1}$$

$$E_{dens} = \frac{HHV_{hydrochar}}{HHV_{DWAS}} \qquad \text{Eq. 5.2.2}$$

$$E_{yield}(\%) = Y_{hyd} \cdot E_{dens} \qquad \text{Eq. 5.2.3}$$

$$H_{C,recov}(\%) = \frac{C_{hydrochar} \cdot hydrochar\ mass}{C_{DWAS} \cdot mass\ of\ DWAS} \cdot 100 \qquad \text{Eq. 5.2.4}$$

5.2.3. Results and discussion

Thermophilic operation

Fig. 5.2.1 shows the time course of selected anaerobic digestions of 10% LF at thermophilic temperature at OLR of 2.5 g COD/L·d and Table 5.2.3 collects the final experimental values of the main variables after 65 d of operation.

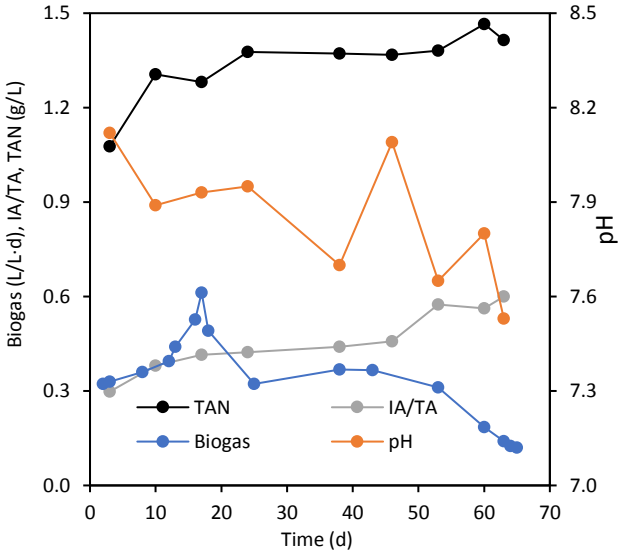

Fig. 5.2.1. Time course of biogas, IA/TA ratio, total ammonia nitrogen and pH along the anaerobic digestion of 10% LF experiment at OLR 2.5 g COD/L·d under thermophilic conditions.

Table 5.2.3. Experimental final values for the main variables influencing the anaerobic digestion of 10% LF mixture ratio operating at OLR 2.5 g COD/L·d under thermophilic conditions.

pH	7.7±0.1
Alkalinity (mg $CaCO_3$/L)	4351±45
IA/TA	0.63±0.01
TVFA (mg COD/L)	7611±31
TAN (mg N/L)	1335±8
FAN (mg N/L)	490±3
Biogas (mL/L·d)	120±10

Under these operational conditions, the pH decreased slightly during the anaerobic treatment (from 8.1 to 7.5), and a high buffer capacity (ca. 4 g $CaCO_3$/L) was observed, which is typical of the fast reactions and high hydrolysis rate of organic matter under thermophilic conditions [15]. This allowed the system to cope with VFA accumulation better. However, the IA/TA ratio increased from 0.3 to 0.6, which suggests overloading of the system through fatty acid accumulation as the likely result of the pH drop observed despite the high buffering capacity of the medium. Thus, the concentration of TVFA amounted to ca. 7.6 g COD/L (21% acetic, 57% propionic, 13% isobutyric+butyric and 9% isovaleric acid). Zhang et al. [32] found high propionate concentrations to result in increased methanogenic inhibition relative to other VFA and to lead to digester failure owing to the complicated biodegradation pathway and the involvement of unusual enzyme systems. This is consistent with the potential overload suggested by the high IA/TA ratio. The TAN concentration in the effluent was around 1.4 g/L, which is close to the inhibitory values obtained by Chen et al. [33], 1.5–7.0 g N/L, especially with unacclimated inoculum. Ammonia nitrogen is an essential nutrient for microorganisms; as ammonium bicarbonate, it additionally buffers the system, which was the main reason for the above-described high total alkalinity. However, thermophilic conditions involved not only an increased temperature, but also an increased pH, which may have displaced the ammonium/ammonia equilibrium to ammonia —acetoclastic methanogens are believed to be most sensitive to FAN [34]. The FAN concentration, 490 mg/L, was fairly lower than the level potentially causing severe inhibition under thermophilic conditions [34], 1 g N/L, although for unacclimated inoculum could inhibit the process. An acceptable initial methane yield (150 mL CH_4/g COD_{added}, equivalent to 0.61 L biogas/L·d) was obtained which, however, fell to very low levels with time. The high TKN values for LF, which were mainly due to the presence of nitrogen-containing

species (viz., refractory pyrazines such as 2-ethyl-5-methylpyrazine and aromatic amines such as 4,5-dimethyl-*o*-phenylenediamine), together with the thermophilic conditions used, resulted in accumulation of these recalcitrant compounds (see Fig. 5.2.2 and Table 5.2.4). On the other hand, 4-methylphenol, 7-methyl-1H-indole and indole, which were detected at low concentrations with the control (PSS) experiment, accumulated with 10% LF (see Fig. 5.2.2). Because indole can be degraded by methanogens and sulfate-reductive microbial populations [35,36], its presence suggests poor digestion leading to terminal process inhibition. By contrast, the presence of phenols, pyrazines and amines can be ascribed to compounds detected in the initial LF [29]. Moreover, as noted earlier, the concentrations of TVFA, TAN and FAN prevented stable operation under thermophilic conditions.

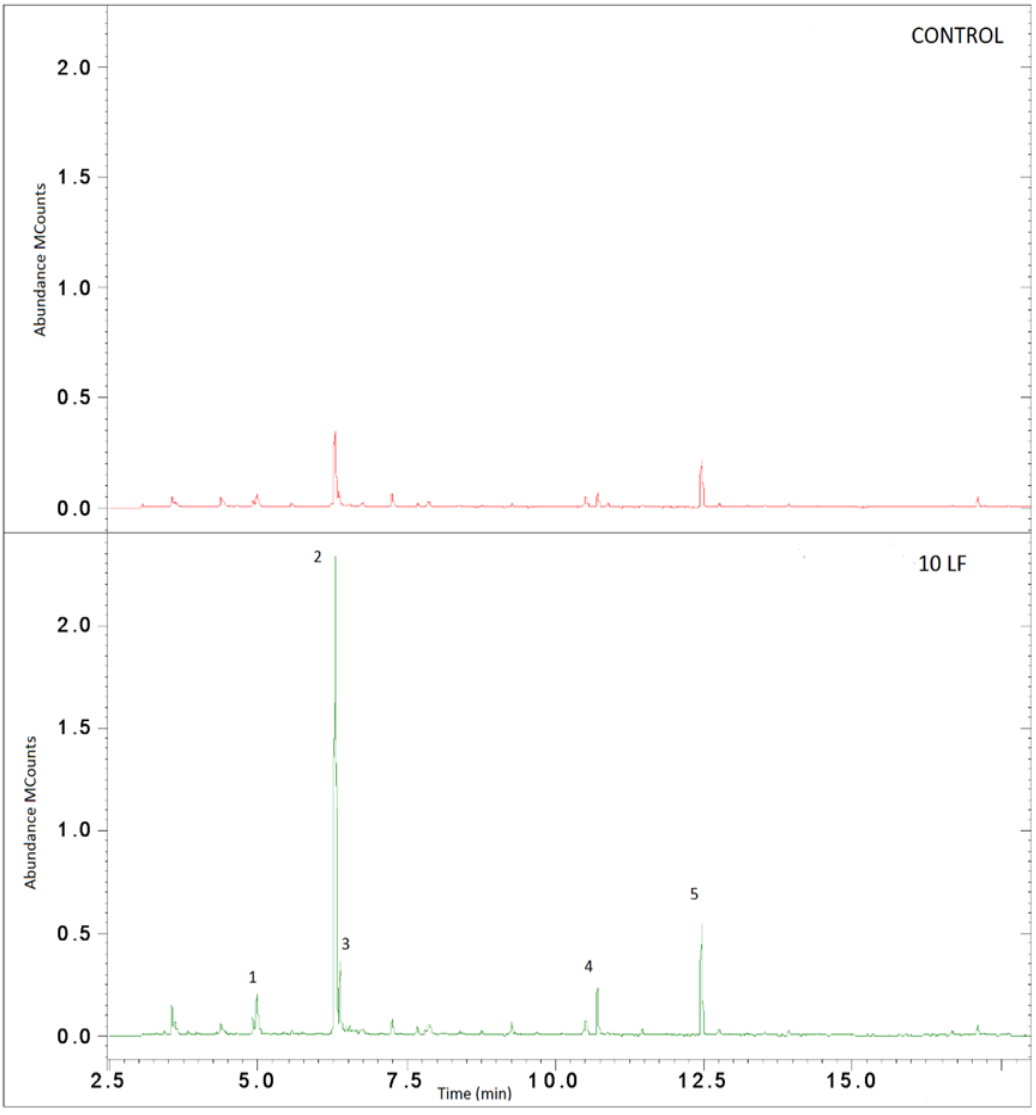

Fig. 5.2.2. GC/MS chromatograms of the control and 10% LF samples under thermophilic temperature and OLR 2.5 g COD/L·d.

Table 5.2.4. Chemical species detected in control and thermophilic digesters operated at OLR 2.5 g COD/L·d.

Compound	Retention time (min)	Peak number
2-ethyl-5-methylpyrazine	5.0	1
4-methylphenol	6.3	2
4,5-dimethyl-o-phenylenediamine	6.5	3
Indole	10.5	4
7-methyl-1H-indole	12.5	5

Mesophilic operation

Fig. 5.2.3 shows the methane yield for the 5% LF, 10% LF and control treatment at the two OLR used (1.5 and 2.5 g COD/L·d). A yield of 172±11 mL CH_4/g COD_{added} (15% more than in the control run) was obtained at OLR of 1.5 g COD/L·d with 10% LF, which reveals increased methane production between both substrates under those specific conditions; with 5% LF, however, the methane yield was similar to that for the control test. Methane production at 2.5 g COD/L·d, 5% LF run (164±2 mL CH_4/g COD_{added}) was fairly similar with 5% LF at the lower OLR, but lower with 10% LF (151±1 mL CH_4/g COD_{added}) than the value obtained at the lower OLR. Villamil et al. [24] obtained a methane yield of 172 mL CH_4/g COD_{added} with a 25% LF mixture under batchwise conditions. Although methane yield tends to be higher under batch conditions than under semi-continuous conditions [37], in this case it was similar pointing out the different LF to PSS ratios.

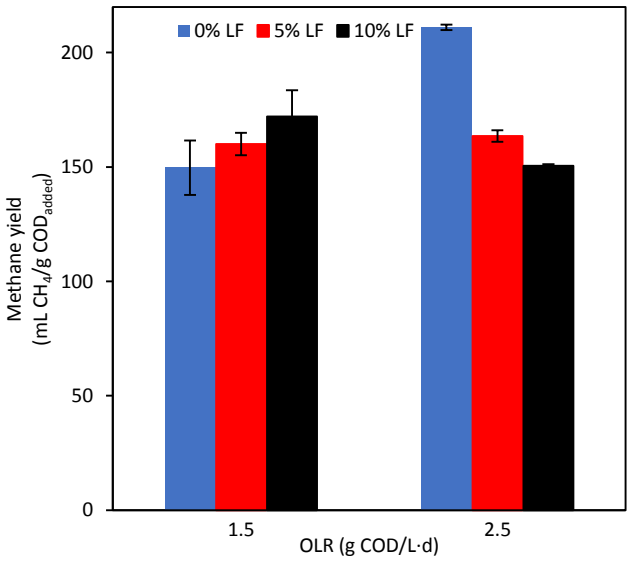

Fig. 5.2.3. Average methane yield vs. organic loading rate for 5% LF, 10% LF and control (0% LF) experiments.

The average methane production at the higher OLR in the control test was 211±1 mL CH_4/g COD_{added}, which is 1.4 times greater than the yield obtained with the lower OLR. Therefore, the methane yield for the PSS tests increased with decreasing HRT. This was a result of the lower OLR providing under optimal conditions for anaerobic digestion of PSS. The methane yield with 10% LF was almost the same with both OLR values, though HRT with the higher OLR is more adequate for full-scale operation and close to the usual value for anaerobic digestion of mixed sludge (20–25 d according to Silvestre et al. [37]). The methane yields obtained at the latter OLR value (HRT 26 d) with 5% LF and 10% LF (151 and 164 mL CH_4 g/COD_{added}, respectively) were higher than those reported by de la Rubia et al. [39] and Choi et al. [40] for mixed sewage sludge digested under identical conditions: 120 and 149 mL CH_4/g COD_{added}, respectively. Therefore, HTC allows the poor degradability of WAS (especially with long sludge retention times) to be circumvented.

The methane yields obtained under the different conditions used were closely related to TVFA contents (Fig. 5.2.4). At the lower OLR, TVFA with 10% LF amounted to 390±38 mg COD/L and consisted mainly of acetic (85%) and propionic acid (15%). This value exceeds that for PSS but falls in the acceptable range for stable reactor operation [15]. The higher OLR (2.5 g COD/L·d) led to a 1.09 times greater TVFA concentration —89% was acetic acid— consistent with the decrease in the methane production by 12%. TVFA concentrations with 5% LF were much higher (up to 1500 mg COD/L) for both OLR, with acetic acid accounting for 900–1200 mg COD/L and propionic acid for 200-400 mg COD/L. This acetate concentration is lower than that reported by Wang et al. [41], ca. 2600 mg COD/L, as inhibitory for methanogenic *Archaea*.

TAN (Fig. 5.2.4) and TA values (Fig. 5.2.4) with 10% LF were almost identical at both OLR levels: ca. 1.2 g TAN/L and 4.75 g $CaCO_3$/L, respectively. Because this TAN concentration is lower than the inhibitory level for the process, the system was not inhibited by ammonia nitrogen [42]. With 5% LF, TAN was ca. 950 mg/L and TA close to 3.8 g $CaCO_3$/L. Both values are lower than those obtained with 10% LF as a result of the increased amount of buffer needed for the high concentration of VFA formed under these conditions, but still higher than the 3.0 g $CaCO_3$/L determined by Yang et al. [43] for the digestion of PSS.

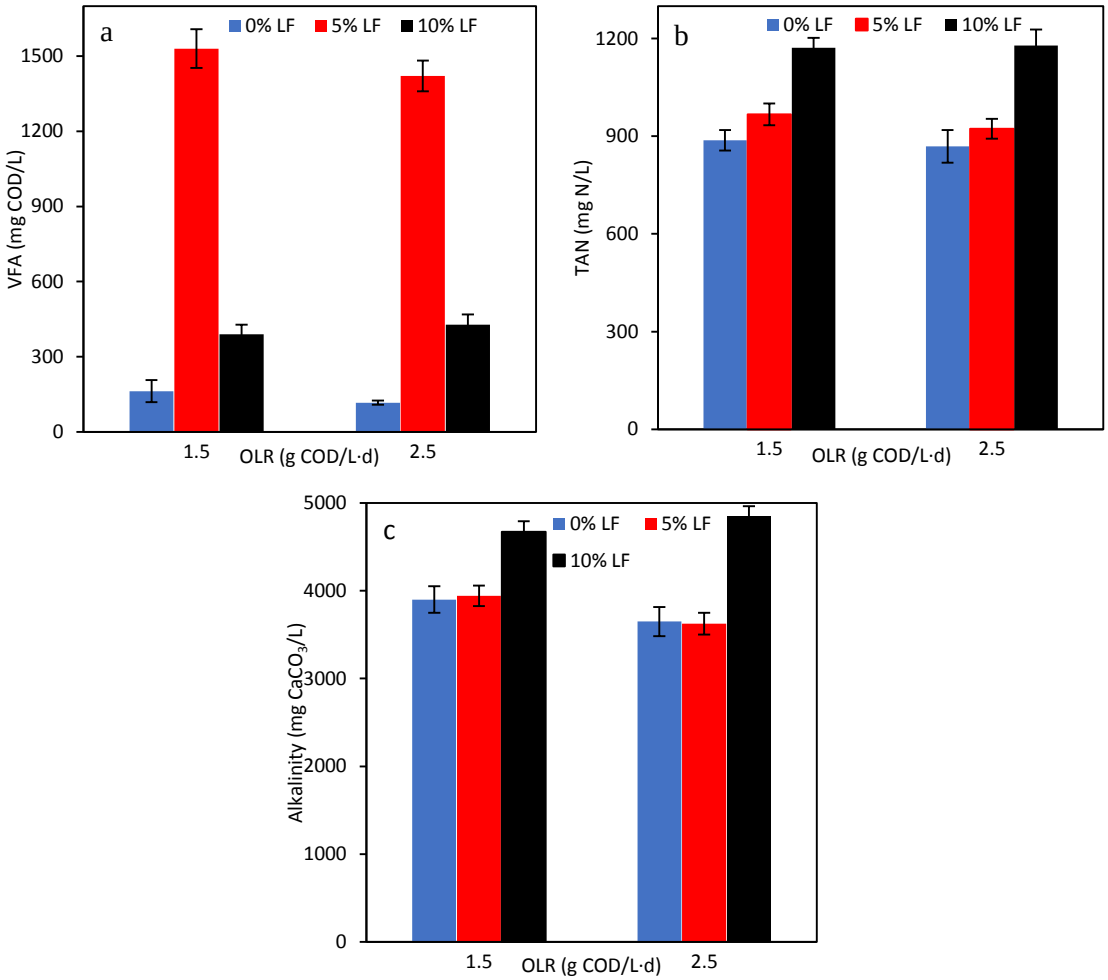

Fig. 5.2.4. Average total volatile fatty acids (expressed as COD) vs. organic loading rate for 5% LF, 10% LF, and control (0% LF) experiments (a); total ammonia nitrogen (expressed as mg N/L), vs. organic loading rate for 5% LF, 10% LF, and control (0% LF) experiments (b); and total alkalinity vs. organic loading rate for 5% LF, 10% LF and control (0% LF) experiments (c).

Methane production was clearly related to organic matter removal as COD (see Fig. 5.2.5). For lower OLR, COD was removed by about 57.2±2.2% from 5% LF, similar to 10% LF (59.2±1.1%) but higher to 10% LF at 2.5 OLR (53.2±2.3%). The slightly less efficient removal of COD from the 10% LF mixture can be ascribed to the increased amount of LF present in the feed and also to accumulation of pyrazines (2-ethyl-3-methyl-pyrazine, 2,3-diethylpyrazine), phenols [2-methyl-6-(2-propenyl)-phenol] and alcohols (3-methyl-2-heptanol) in the effluent (Fig. 5.2.6 and Table 5.2.5). The COD removal values are consistent with that obtained by de la Rubia et al. [39], 56.1%, by treating mixed sewage sludge under mesophilic conditions at OLR of

2.5 g COD/L·d (HRT = 27 d); (i.e., under conditions similar to those used in our tests at the higher OLR), but greater than that reported by Choi et al. [40], 42%, also operating at OLR of 2.5 g COD/L·d. On the other hand, COD removal at both OLR levels in the control treatment was ca. 63% and consistent with the value of Yang et al. [43] for the digestion of 100% of PSS. VS concentrations were reduced by at least 54% at both OLR levels and mixture ratios, which is higher than the acceptable value for industrial sludge digestion under mesophilic conditions: 40% reduction [15].

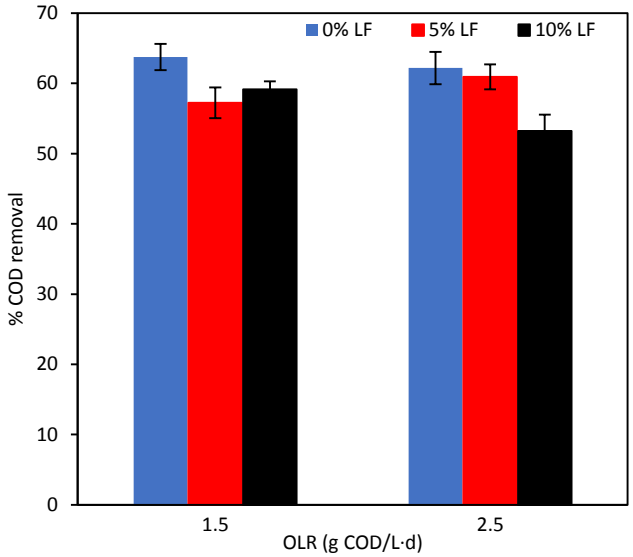

Fig. 5.2.5. COD removal vs. organic loading rate for 5% LF, 10% LF and control (0% LF) experiments.

Table 5.2.5. Chemical species detected in control and mesophilic digesters operated at OLR 1.5 g COD/L·d.

Compoud	**Retention time (min)**	**Peak number**
2-ethyl-3-methyl-pyrazine	6.0	1
2,3-diethylpyrazine	7.5	2
3-methyl-2-heptanol	8	3
2-methyl-6-(2-propenyl)-phenol	10.5	4
7-methyl-1H-indole	13.7	5

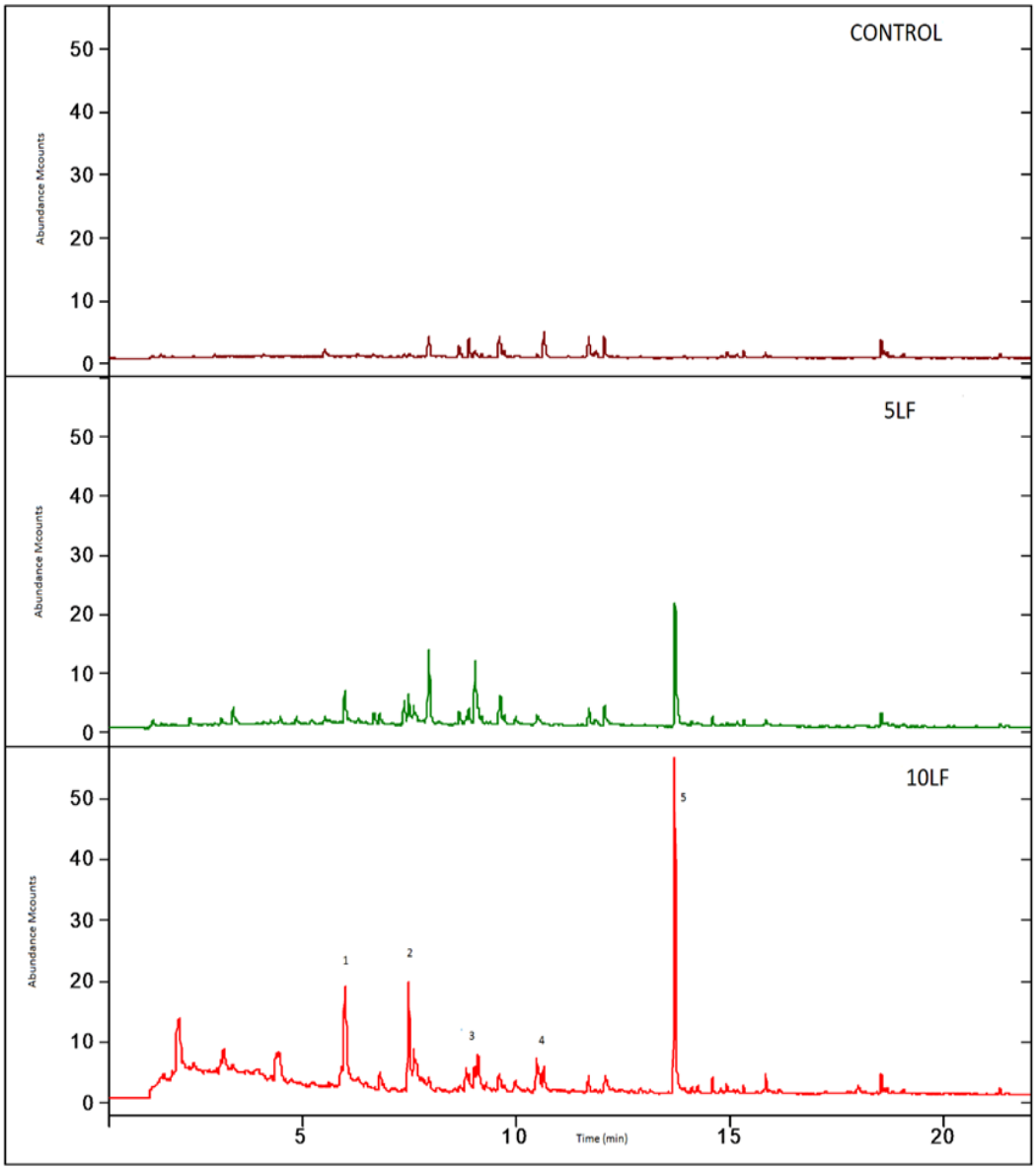

Fig. 5.2.6. GC/MS chromatograms of the control (0% LF), 5% LF and 10% LF samples under mesophilic temperature and OLR 1.5 g COD/L·d.

Regarding mesophilic performance, an increased proportion of LF in the mixture with PSS seemingly hinders anaerobic digestion relative to PSS alone owing to the high concentration of inhibitory compounds formed and accumulated. In fact, more than 10% LF in the mixture made the process inviable while using exactly a mixture of 10% LF required operating at low OLR, which increased HRT and finally, lead to the anaerobic digester to an unusual operation condition (44 d). Lower proportions of LF such as 5% allow operation at higher OLR levels and with HRT values (26 d) in the range commonly accepted (20-40 d). Therefore, hydrothermal carbonization not only provides

a hydrochar with a substantial HHV (ca. 22 MJ/kg) but also improves anaerobic digestion yields for dewatered waste activated sludge.

Energy balance of the proposed approach (HTC+anaerobic digestion)

The hydrochar yield reached, applying the conditions set out in Section 5.2.2, was 40.3%. The proximate analysis of DWAS and hydrochar are shown in Table 5.2.2. The carbonization process reduced the fixed carbon of hydrochar from 7.3 to 4.4%, in addition the volatile matter was converted into other products, such as liquid fraction and CO_2, as He et al. [44] observed, being reduced from 73.6 to 65.4%. As a result, the ash content increased from 13.7 to 19.7% due to the excess loss of VM. Parshetti et al. [45] determined 41.72% VM and 40.46% of ash content after HTC of DWAS at 250 ºC for 15 min using a stirred reactor of 0.5 L. High ash content and low fixed carbon are usually obtained after municipal wastewater streams (PSS, DWAS, mixed sludge, and digestate) [18,44-46].

The HHV obtained in this work (21.6 MJ/kg) was higher than those reported for PSS (18.0 MJ/kg), mixed sludge (18.6 MJ/kg), DWAS (15.82;19.8 MJ/kg), and digestate (11.35-15.09 MJ/kg) operating at similar temperatures (200-220 ºC) than used in our study [12,18,44-48]. The anaerobic digestion, previously subjected, can explain the low value of hydrochar from digestate. However, it is difficult to compare directly the hydrochar HHV reported in the literature and those measured in this study, since reaction time, reactor design, initial solids concentration, and temperature, influence the degree of carbonization. In addition, the HHV of hydrochar is higher than those of the brown coal and lignite are (<17.4 MJ/kg). Moreover, significant energy densification (Eq. (5.2.2)) up to 1.23 occurred because of decarboxylation and dehydration reactions, increasing the carbon content a 12% respect to the feedstock while a carbon recovery of 41.9% for hydrochar was reached. The energy yield (Eq. (5.2.3)), which relates the energy remaining within the hydrochar to that of the original biomass, reached 50.1%. A lower value than the ones obtained by Danso-Boateng et al. [12] (73%) and Aragón-Briceño et al. [18] (70%) for HTC of PSS and digestate, respectively, at similar temperature and reaction times than used in our study. These results show the verified conversion of DWAS to energy through HTC by potential applications of hydrochar (the main product of the HTC process) as a solid fuel, while the remaining carbon in the liquid fraction can be recovered as biogas by anaerobic digestion.

Table 5.2.6 compares the energy production from feedstock after conventional anaerobic digestion of mixed sludge with the pretreatment by thermal hydrolysis before anaerobic

digestion and the overall energy produced from the hydrochar obtained after HTC (of digestate or DWAS) plus anaerobic digestion or co-digestion of the obtained liquid fraction. The valorization of mixed sludge by conventional anaerobic digestion [39,49] is limited, due to the low biodegradability of waste activated sludge as has been commented above. The energy produced from methane by co-digestion of the LF and PSS mixtures is slightly better than the obtained digesting PSS alone at low OLR, but lower under 2.5 g COD/L·d. However, taking into account the additional energy that can be obtained from the hydrochar (8.76 MJ/kg feedstock), the overall energy produced is between 4.1 and 4.4 times the generated by conventional anaerobic digestion of mixed sludge. Aragón-Briceño et al. [18] found slightly lower values of overall energy produced for hydrothermal carbonization of digestate sewage at 220 ºC for 30 min followed by mesophilic anaerobic digestion of slurry and liquid fraction produced. However, a higher ash content of hydrochar (45.1%) was reported which limit the application of hydrochar as solid fuel. Comparing with thermal hydrolysis [50], up to 2-fold increase in the overall energy produced was reached with the process applied in this study. These findings suggest that the integral approach for sewage sludge management proposed in this work can be a feasible option for the valorization of this feedstock in an urban WWTP, as well as the relevance of applying the hydrochar as solid fuel since up to 43% the overall energy produced for run OLR 1.5 g COD/L·d with 10% of LF, depends on this product. Therefore, the energy balance of the proposed approach is clearly improved.

Table 5.2.6. Energy production from sewage sludge

Energy produced from feedstock (MJ/kg)				
	CH_4	**Hydrochar**	**Overall energy**	**References**
AD of mixed sludge	4.61; 4.45	-	4.61	[39,49]
Thermal hydrolysis+AD	10.13	-	10.13	[50]
AD + HTC + AD*	8.36	10.52	18.88	[18]
OLR 1.5 g COD/L·d, PSS	10.35	-	10.35	This study
OLR 1.5 g COD/L·d, 5% LF	10.96	8.76	19.72	
OLR 1.5 g COD/L·d, 10% LF	11.70	8.76	20.46	
OLR 2.5 g COD/L·d, PSS	14.56	-	14.56	
OLR 2.5 g COD/L·d, 5% LF	11.24	8.76	20.00	
OLR 2.5 g COD/L·d, 10% LF	10.27	8.76	19.03	

*HTC of digestate (220 ºC, 30 min) followed by AD of the liquid fraction
HHV of methane: 35.8 MJ/m^3

5.2.4. Conclusions

HTC of dewatered waste activated sludge and anaerobic co-digestion of PSS and LF provide an efficient treatment for sewage sludge. Under thermophilic conditions, the co-digestion showed progressive inhibition evidenced by indole accumulation; also, VFA and NH_3 concentrations are high, and methane yield low. The mesophilic regime, operated at low OLR (1.5 g COD/L·d) led to a 1.15 times higher methane yield with 10% LF than with the control treatment (0% LF), at 2.5 g COD/L·d enhances methane yields higher than those reported for mixed sludge. COD removal was at least 53% irrespective of the operating conditions. Meanwhile, TAN, alkalinity and VFA fell within the ranges for stable operation of the digester. Therefore, applying HTC to dewatered waste activated sludge and co-digesting PSS and LF provides an improved management method for this waste as well as a positive energetic balance (hydrochar+biogas) around 2.0 times higher than with control treatment and 4.4 times higher than with conventional anaerobic digestion of mixed sludge.

5.2.5. References

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Chapter: 6

The co-digestion of the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge and the organic fraction of municipal solid waste in batch experiments

6.1

Mesophilic anaerobic co-digestion of the organic fraction of municipal solid waste with the liquid fraction from hydrothermal carbonization of sewage sludge

M.A. De la Rubia, J.A. Villamil, J.J. Rodriguez, R. Borja, A.F. Mohedano, Mesophilic anaerobic co-digestion of the organic fraction of municipal solid waste with the liquid fraction from hydrothermal carbonization of sewage sludge, Waste Manag. 76 (2018) 315–322

Abstract

In the present study, the influence of substrate pre-treatment (grinding and sieving) on batch anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) was first assessed, then followed by co-digestion experiments with the liquid fraction from hydrothermal carbonization (LF) of dewatered waste activated sludge (DWAS). The methane yield of batch anaerobic digestion after grinding and sieving (20 mm diameter) the OFMSW was considerably higher (453 mL STP CH_4/g VS_{added}) than that of untreated OFMSW (285 mL STP CH_4/g VS_{added}). The modified Gompertz model adequately predicted process performance. The maximum methane production rate, G_{max}, for *ground* and *sieved* OFMSW was 2.4 times higher than that of untreated OFMSW. The anaerobic co-digestion of different mixtures of OFMSW and LF of DWAS did not increase the methane yield above that of the anaerobic digestion of OFMSW alone, and no synergistic effects were observed. However, the co-digestion of both wastes at a ratio of 25% LF provides a practical waste management option. The experimental results were adequately fitted to a first-order kinetic model showing a kinetic constant virtually independent of the percentage of LF (0.52–0.56 d^{-1}) and decreasing slightly for 100% LF (0.44 d^{-1}).

6.1.1. Introduction

Anaerobic digestion is a well-proven and mature technology for producing methane-rich biogas from the decomposition of organic wastes. Because of the energy efficiency of this technology, it has been used for treating biodegradable wastes, such as the organic fraction of municipal solids wastes (OFMSW), wastewater treatment biosolids, and a number of food and beverage wastes [1]. Over 17,000 biogas plants have been constructed in Europe, primarily in Germany (over 10,000 plants), followed by Italy and France [2]. The majority of the biogas plants (72%) are powered by agricultural resources, and the remainder use mainly organic waste substrates and sewage sludge [3].

Anaerobic digestion of single substrates presents some drawbacks linked to characteristics of the substrates. Anaerobic co-digestion, the simultaneous digestion of two or more substrates, is a practical option to overcome the drawbacks of mono-digestion and to improve a plant's economic feasibility [4]. Anaerobic co-digestion has many advantages compared to digestion of wastes alone: it improves the process stability, increases organic loading rates and methane yield, dilutes toxic compounds, and balances solid content and nutrients, all of which allow for treatment of different wastes

in one facility [5,6]. Recently, the main use of anaerobic co-digestion has been for co-digestion of OFMSW and thickened sewage sludge [4,7].

In 2013, global municipal solid waste production was approximately 1300 million t/yr [8], and it is estimated that in 2025 the production will rise to 2200 million t/yr, with approximately 46% organic content [9]. OFMSW is characterized by a high C:N ratio resulting from the presence of paper materials and other carbon-rich substances [10]. However, sewage sludge has a relatively low C:N ratio, ranging from 6:1–13:1. Appropriate mixing ratios of sewage sludge and OFMSW can provide an optimum C:N ratio (20:1–30:1) for anaerobic digestion [11]. Sludge is also rich in other macro- and micro-nutrients that stimulate the anaerobic digestion process [12].

Anaerobic digestion has become the preferred option to valorize sewage sludge. In recent decades, thermal treatments (e.g., pyrolysis or gasification) that require pre-dyed feedstock have also been used for treating sewage sludge. Hydrothermal carbonization (HTC) is a relatively new process for wet biomass valorization, and is usually performed at temperatures lower than 375 ºC and pressures of 4–22 MPa [13]. This technology is very promising for valorizing dewatered waste activated sludge (DWAS), and produces hydrochar with a high heating value [14]. The liquid fraction obtained is characterized by a high chemical oxygen demand (COD) (90–100 g/L) and has a total Kjeldahl nitrogen (TKN) value of 8.7 g N/L with a C:N ratio of 7:1 [15]. These are similar to the values observed for thickened sewage sludge [11]. Reports on the potential to produce methane from the liquid fraction from hydrothermal carbonization (LF) are limited. Previous studies have primarily focused on the results from LF of lignocellulosic residues [16,17]. Moreover, to date, no study has investigated the co-digestion of OFMSW and LF of DWAS. The aim of this work was to study anaerobic co-digestion of the LF of DWAS and OFMSW using different co-substrate ratios. Biochemical methane potential (BMP) tests were conducted to determine the effects of the mixture co-substrate ratio under mesophilic temperatures on methane yield. The effects of substrate pre-treatment, after grinding and sieving, on anaerobic digestion of the OFMSW are also reported.

6.1.2. Materials and methods

Inoculum source

The anaerobic inoculum was obtained from the anaerobic digestate collected from a mesophilic reactor that treats the OFMSW from a municipal solid waste treatment plant (MSWTP) located near Madrid, Spain. The main characteristics of this digested solid

waste were: pH, 8.2±0.1; total solids (TS), 136.8±0.6 g/kg; volatile solids (VS), 70.7± 0.8 g/kg; and total chemical oxygen demand (TCOD), 84.2±6.5 g/L.

Substrate characteristics

a. Influence of substrate pre-treatment

The sample of OFMSW was taken from the waste reception area of the aforementioned MSWTP. Although the solid waste delivered to the plant is source-segregated at the household level, it still contained considerable amounts of plastic, paper, cardboard, metal, and glass. About 100 kg of OFMSW was manually sorted and the non-OFMSW portion was removed. Part of the prepared sample of OFMSW (*raw OFMSW*), was ground in a mill (*ground OFMSW*). In addition, a portion of the shredded organic waste was sieved to a final particle size of <20 mm (*ground+sieved OFMSW*), increasing the homogeneity of the substrate. A commercial sieve (Orto Alresa OASS203) was used to shred and classify the OFMSW by using a 20 mm screen mesh (Cisa, serial number 151534.2). The main characteristics of the substrates are summarized in Table 6.1.1.

Table 6.1.1. Main characteristics of the OFMSW substrates: *raw*, *ground* and *ground+sieved*

Substrate	TS (g/kg)	VS (g/kg)	COD (mg O_2/g TS)
Raw	498.7±6.9	288.9±5.7	-
Ground	443.7±1.7	281.8±9.8	-
Ground+Sieved	466.5±3.0	279.9±13.3	1163±7

b. Co-digestion of OFMSW with LF of DWAS

Co-substrate 1. The *ground+sieved* OFMSW used to assess the influence of substrate homogeneity was selected as the first co-substrate. A more detailed characterization of this specific fraction, than showed in Table 6.1.1., was carried out (average values of three determinations±standard deviations), including the elemental composition: 24.52±2.89% C, 1.64±0.46% H, 1.90±0.19% N, 0.13±0.05% S; carbohydrates, 2590.1±131.2 mg/L; proteins, 2035.5±70.1 mg/L; and volatile fatty acids (VFA), 2045.4±38.3 mg COD/L.

Co-substrate 2. The LF, used as co-substrate 2, was obtained from hydrothermal carbonization of DWAS (85% moisture), which was collected from a full-scale membrane bioreactor that treats industrial wastewaters from a cosmetics factory. The co-substrate was maintained at -20 ºC until use. HTC of 1.5 kg of DWAS was performed in a ZipperClave® 316 stainless steel pressure vessel with a working volume of 4 L

(127 mm of inside diameter and 312 mm of inside length) and a maximum allowable working pressure of 151 bar at 232 ºC. The reactor is equipped with a Rushton impeller (diameter: 50.8 mm) and a bottom flush valve. The temperature (208 ºC) and stirring rate (150 rpm) were controlled using an (IB62) Iberfluid controller. The operating temperature was reached via a heating rate of 3 ºC/min, maintained for 1 h. The reaction was stopped by cooling with an internal heat exchanger using tap water. The liquid fraction was recovered by centrifugation (3500 rpm for 1 h) and filtration (0.45 µm); then was maintained at 4 ºC until anaerobic digestion tests were performed.

The main characteristics and composition of this LF (average values of three determinations±standard deviations) were: pH, 5.1±0.1; soluble COD (SCOD), 109.6±0.9 g/L; TS, 55.7±0.5 g/L; VS, 46.2±0.5 g/L; total organic carbon (TOC), 42.6±0.9 g/L; TKN, 8.7±0.1 g/L; carbohydrates, 2237.3±31.9 mg/L; proteins, 5420.5±116.5 mg/L and VFA, 2748.6±57.3 mg COD/L. Fig. 6.1.1 depicts a representative GC/MS chromatogram showing its fairly complex composition (Table 6.1.2).

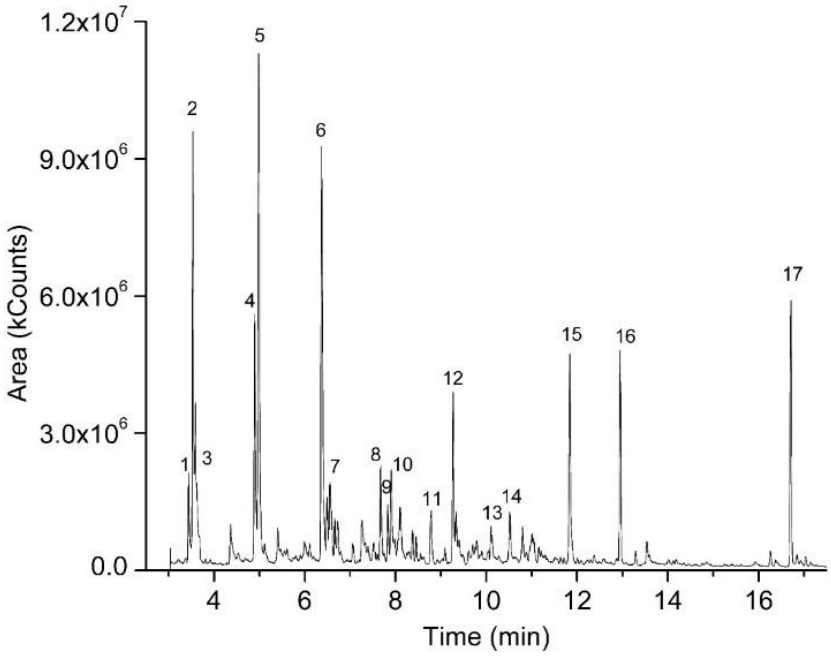

Fig. 6.1.1. GC/MS of the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge.

Table 6.1.2. Species identified by GC/MS in the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge (see Fig. 6.1.1 for peaks)

Compound	**Peak number**	**Total peak area (%)**
Aldehydes		
4-Methoxycinnamaldehyde	16	6.5
Nitrogenated compounds		
4-Pentyloxyaniline	2	5.1
1H-Pyrrole-2-carboxaldehyde, 1-methyl-	3	5.2
Pyrazine, 2-ethyl-5-methyl-	4	3.6
Benzenamine, 3-methoxy-	5	11.8
4,5-Dimethyl-ortho-phenylenediamine	6	10.8
2,3-Diethylpyrazine	7	1.5
Pyrazine, 2,5-dimethyl-3-propyl-	11	5.2
2(1H)-Quinoxalinone	13	0.9
1-Butanamine	14	1.2
Oxygenated aromatics		
Furan, 2,5-dimethyl-	1	1.4
Benzene, 1,2,4,5-tetramethyl-	8	2.0
Phenol, 2,3,5,6-tetramethyl-	9	0.9
Benzoic acid, 4-formyl-	10	2.1
Phenol, 2-methyl-6-(2-propenyl)-	12	4.4
Phenol, 2-methyl-5-(1-methylethyl)-	15	5.4
Benzophenone	17	4.2

Batch anaerobic experiments

Experiments were conducted in an automatic methane potential test system (AMPTS), which is a laboratory-scale batch methane-potential analyzer developed by Bioprocess Control AB (Lund, Sweden) following the procedure described elsewhere [18–20]. This devise registered only methane flow because other gas components, such as CO_2 and H_2S, were removed by an alkaline solution. A data acquisition system was incorporated.

a. Experiment to assess the influence of substrate homogeneity

The reactors (total volume: 1 L) were maintained at 35±1 ºC, and initially charged with the inoculum by maintaining a concentration of 15 g VS/L. The inoculum to substrate ratio (ISR) was maintained at 2 (VS basis) to avoid acidification, because anaerobic digestion can be inhibited by accumulation of VFA at ISR lower than 1 [15, 21-23]. Therefore, 7.5 g VS/L of OFMSW was added to every batch reactor for the three fractions studied. Fifty milliliters of stock mineral medium solution (composition described in

Villamil et al. [15] was added, followed by deionsed water, to achieve the desired working volume of 225 mL. The reactors were flushed with N_2 to establish an anaerobic condition.

b. Experiment of co-digestion of OFMSW and LF

Co-digestion experiments were conducted maintaining the ISR at 2 on a VS basis (1.75 on a COD basis), using different mixing ratios of OFMSW and LF, on a COD basis: 100% OFMSW, 75% OFMSW-25% LF, 50% OFMSW-50% LF, 25% OFMSW-75% LF, and 100% LF. Throughout this Ph.D. thesis, these co-substrates are referred to as 0% LF, 25% LF, 50% LF, 75% LF, and 100% LF, respectively.

To determine the composition of the biogas from the co-digestion experiment, 120 mL glass serum vials (working volume of 60 mL) were filled with the same proportion of inoculum, substrates, and basal medium. Before sealing the vials with rubber stoppers and metallic crimps, the suspensions were flushed with N_2 for 3 min to establish anaerobic conditions. The vials were maintained at a mesophilic temperature (35±1 ºC) using a thermostatic water bath shaker (80 rpm). All the experiments were run until no significant gas production was observed, suggesting that biodegradation was essentially completed. This was confirmed with controls of starch (≈350 mL CH_4/g COD_{added}). Triplicate blank samples with no substrate were run to determine the amount of background methane originating from the inoculum alone.

Analytical methods

The inoculum and OFMSW were characterized by dry matter, moisture, VS, and ash according to Standard Methods 2540B and 2540E [24]. TCOD was determined by the method proposed by Raposo et al. [25]. This analysis used 1 mL (liquid sample) or 250 mg (solid sample), 20 mL $K_2Cr_2O_7$ 1.2 N, 30 mL H_2SO_4–Ag_2SO_4, and the final solution was titrated with ferrous ammonium sulfate 0.5 N. Elemental analysis, was determined using a Leco CHNS-932 (Model No: 601-800-500) elemental analyzer, following the manufacturer's standard procedures.

The LF of DWAS was characterized by pH (using a model Crison 20 Basic pH meter), SCOD (using the closed digestion and colorimetric standard method 5220D [24], TOC (with an automatic analyzer TOC-VCPN, Shimadzu), and TKN (determination described in Villamil et al. [15]). The identification of species was performed by gas chromatography/ion trap mass spectrometry (GC–MS; CP-3800/Saturn 2200) with an autosampler injector (Varian CP-8200), and a solid phase microextractor, (Carbowax/Divinylbenzene Yellow-Green). A Factor Four VF-5ms capillary column (30 m long, 0.25 mm diameter) was used. Sample injection was carried out with split-less

at 220 ºC, using He as carrier gas. The temperature program used in the GC/MS analyses ramped as follows: 40 ºC for 15 min and 15 ºC/min until 250 ºC. The compounds were identified using the NIST 2008 Library.

Both co-substrates were characterized by carbohydrates and proteins by the methods proposed by Dubois et al. [26] and Lowry et al. [27], respectively. Individual VFA concentrations (from acetic to heptanoic, including iso-forms) were determined by gas chromatography (GC) (Varian 430-GC) equipped with a flame ionization detector (FID) and a capillary column filled with Nukol (polyethylene glycol modified by nitroterephthalic acid). Prior to injection, 900 µL of the sample was mixed with 150 µL of H_3PO_4 (1:2 V:V) to adjust pH below 2.0 and 150 µL of a solution of crotonic acid (2000 mg/L) as an internal standard. This mixture was centrifuged to remove any solids and transferred to a 1500 µL gas GC vial. The sample injection volume was 1 µL. The temperatures of the injector and detector were maintained at 200 and 250 ºC, respectively, while the column temperature was increased from 120 to 160 ºC with an increasing rate of 10 ºC/min.

As stated previously, volumetric and manometric experiments were conducted for co-digestion assays. For the manometric method [28], biogas production was determined by measuring the pressure increase in each vial using an electronic pressure monitor (ifm, PN 7097). This was measured daily during the first 3 d and eight more times for the remainder of the incubation period. It was expressed at standard temperature and pressure (STP: 273 K, 1 bar). Biogas was subsequently exhausted to re-establish atmospheric pressure. The gas composition (H_2, H_2S, CO_2, and CH_4) was determined by gas chromatography separation (Thermo Scientific Trace 1310) with an 8 ft. × 1/8 in. SS column packed with HayeSep Q 80/100 mesh and a thermal conductivity detector (TCD). The injection volume was 1 mL. The temperatures of the injector and detector were maintained at 110 and 150 ºC, respectively. Helium was used as the carrier at a flow rate of 30 mL/min. A standard gas (Praxair, S.A; composition: 7.35% H_2; 3.01% H_2S; 59.84% CH_4, and 29.8% CO_2) was used for system calibration.

6.1.3. Results and discussion

Influence of substrate pre-treatment on methane potential

Fig. 6.1.2 shows variations in the accumulated methane yields (mL STP CH_4/g VS_{added}) with time for the *raw*, *ground*, and *ground+sieved* OFMSW substrates. Lag periods of

8-14 d were observed for the three substrates tested, after which exponential increases in methane production were detected until reaching a final maximum value, which coincided with the ultimate methane yield for each case studied. These values were 285, 249, and 453 mL CH_4/g VS_{added} for *raw*, *ground*, and *ground+sieved* OFMSW substrates, respectively.

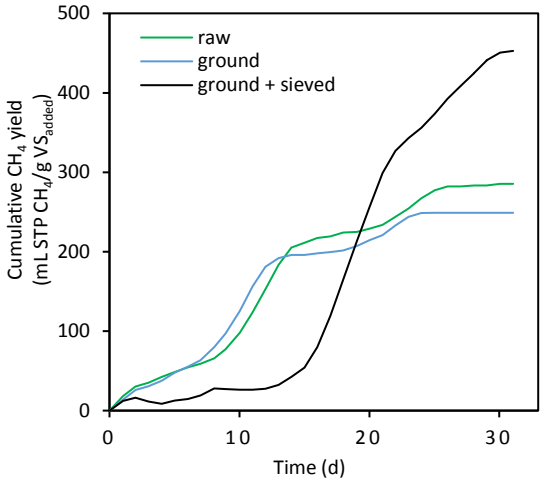

Fig. 6.1.2. Time-course of methane yield for raw, ground and ground+sieved OFMSW substrates.

The values reported in the literature indicate that OFMSW can produce approximately 300–500 mL CH_4/g $VS_{added,}$ with an average methane yield of 367 mL CH_4/g VS_{added}, depending on the source and type of OFMSW. Specifically, Curry and Pillary [29] obtained methane yields in the range 310–490 mL CH_4/g VS_{added} with anaerobic digestion of OFMSW, while Davidsson et al. [30] and Karnchanawong and Uparawanna [31] achieved methane production of 300–400 mL CH_4/g VS_{added}, respectively. More recently, Abudi et al. [32] reported yield coefficient values of 214 mL biogas/g VS in anaerobic digestion experiments of *raw* OFMSW carried out in batch mode at a mesophilic temperature (37 ºC). All these values were lower than those obtained in the present study for anaerobic digestion of *ground + sieved* OFMSW.

There is wide variability in the BMP from OFMSW, depending on the separation operations carried out on this substrate. The highest methane production was achieved when the waste was more homogeneous, that is, when the waste was subjected to grinding and sieving. This type of mechanical pretreatment reduces the particle size and increases the specific surface area available to the anaerobic microorganisms. This improves

solubilization and allows the process rate to increase. In addition, this pretreatment generally facilitates the release of carbon from the organic matter contained in the substrate, increasing its biodegradability, and thereby resulting in higher yields. These results agree with those obtained by Hajji and Raji [33], who evaluated particles of 10, 20, 30, and 100 mm diameter in anaerobic digestion of OFMSW under mesophilic conditions (40 ºC) with retention time of 21 d. The results showed a correlation between particle size and biogas production, with optimum production recorded for smaller particle sizes, and improvement in the biogas yield of approximately 20% for 10 mm particles.

Similarly, after efficient mechanical sorting of OFMSW, a reduction of biodegradable organics in particles <10 mm, and removal of any remaining glass, it was demonstrated that the composition of the resulting sorted waste was close to a source-sorted organic fraction. The methane yields obtained for the last waste samples were comparable to that from raw biodegradable organics [34]. In this sense, pretreatment of OFMSW based on a prototype optical sorter, a wet-crusher, and a hydrocyclone-decanter (which uses near-infrared spectroscopy) could increase the organic matter content from 40 to 60% in a more efficient and less energy-demanding way than methods used in conventional systems [35]. After this pre-treatment, methane yields of 480–560 mL CH_4/g VS were obtained, which were somewhat higher than those obtained in the present work. For other solid substrates such as two-phase olive pomace, for which mechanical pre-treatment by milling was used to obtain grain size of 3 mm in diameter, there was an increase in the maximum methane production rate from 6.99 (untreated waste) to 11.25 mL CH_4/g VS·d (pre-treated waste) [36].

The modified Gompertz kinetic model is a sigmoid function that is used as a mathematical model for a time series, where growth is the slowest at the beginning and at the end of a given time period [37]. It is one of the best functions for predicting the biogas production in batch-mode anaerobic digestion processes. Many researchers have studied the application of first-order and second-order kinetic models, and other models, and found that the modified Gompertz model has one of the best fits to data pertaining to biogas or methane production as a function of time under anaerobic processes conducted in batch mode. In addition, the modified Gompertz model was calibrated and examined using many experimental data [36-38]. Li et al. [39] used the modified Gompertz model to study the effects of the feedstock-to-inoculum ratio and substrate concentration on the batch

mesophilic anaerobic digestion of OFMSW. This was done using a single-factor experiment and uniform-design multi-factor experiments. The results showed that substrate concentration had a greater influence on the maximum biogas yield and maximum biogas production rate, while the feedstock-to-inoculum ratio had a lesser or non-existent effect on those parameters.

In the modified Gompertz model, the cumulative methane production is related to the digestion time through the following equation:

$$G(t) = G_{max} \cdot exp\left[-exp\left(\frac{\mu}{G_{max}} \cdot (\lambda - t) \cdot e^{1} + 1\right)\right] \quad \text{Eq. 6.1.1}$$

where:

G(t) is the cumulative methane production at time *t* (mL CH_4/g VS_{added}), G_{max} is the maximum methane production or methane yield potential (mL CH_4/g VS_{added}), μ is maximum methane production rate (mL CH_4/g VS_{added}·d), λ is the lag time (d), *t* is the digestion time (d) at which the cumulative methane production is calculated, and e is the exp (1)= 2.7183.

The parameters G_{max}, μ, and λ were calculated for each of the runs using the non-linear regression approach with SigmaPlot 11.0 software. Table 6.1.3 shows the values of the model parameters obtained from the modified Gompertz model for the three substrates assayed. Similar to the results of the experimental maximum methane production values, and relative to the G_{max} value obtained for *raw* OFMSW, the theoretical G_{max} value decreased by 17.6% and increased by 57.5% for *ground* and *ground+sieved* OFMSW, respectively. Therefore, a considerable increase in the biodegradability of the substrate was observed when the substrate was homogenized and sieved to achieve lower particle sizes [32]. In addition, the difference between the measured and predicted methane yields were found to be only 6.3, 3.6, and 4.5% for *raw, ground,* and *ground+sieved* OFMSW substrates, respectively, which demonstrated a good fit of the experimental results to the proposed model. The high values of the determination coefficients (R^2) and the low values of the standard errors of the estimate (Table 6.1.3) also showed the excellent fit of the experimental results to the modified Gompertz model.

Table 6.1.3. Parameters of the modified Gompertz model for the three substrates studied (*Raw*, *Ground* and *Ground+Sieved* OFMSW).

Substrate	G_{max} (mL CH_4/g VS)	μ (mL CH_4/g VS·d)	λ (d)	R^2	S.E.E.
Raw	302.3±1.7	15.7±0.1	2.42±0.06	0.983	12.3
Ground	248.9±0.8	17.3±0.1	2.30±0.05	0.985	10.6
Ground+Sieved	476.1±3.0	39.1±0.3	1.36±0.04	0.989	14.8

R^2: coefficient of determination; S.E.E.: Standard error of estimate.

The maximum methane production rate, μ, for *ground* and *ground+sieved* OFMSW was 1.1 and 2.4 times higher, respectively, than the values obtained for *raw* OFMSW. Therefore, the homogenization and screening of this substrate to particle sizes less than 20 mm increased the rate of anaerobic digestion of OFMSW, and accelerated the methane production rate. This high μ value (39.1 mL CH_4/g VS·d) exceeded the one reported by Abudi et al. [32] in the batch anaerobic digestion of untreated OFMSW (27.7 mL CH_4/g VS·d). The results obtained in the present work agree with those obtained by Donoso-Bravo et al. [36] for the anaerobic digestion of two-phase olive pomace, for which the μ value was 1.6 mL CH_4/g VS·d higher than that for the untreated waste, when the substrate was milled to a particle size of less than 3 mm. The pre-treatment of grinding and sieving reduces the particle size, increasing the specific surface area available to the anaerobic microorganisms and, at the same time, the methane production rate.

The lag time (λ) value for *ground+sieved* OFMSW substrate (1.36 d) was 44% lower than that obtained for raw OFMSW substrate (2.42 d), which also demonstrates the advantage and benefit of the pre-treatment of this waste prior to treatment with anaerobic digestion. The lag value obtained for *raw* OFMSW was higher than that obtained by Amiri et al. [37] for the batch anaerobic co-digestion of OFMSW, leachate, and sludge (0.2–0.5 d).

Mesophilic anaerobic co-digestion of OFMSW with LF of DWAS

A study of the anaerobic co-digestion of different mixtures of OFMSW and LF of DWAS (25% LF, 50% LF, and 75% LF), as well as of the corresponding single substrates (0% LF and 100% LF) was conducted. Fig. 6.1.3 shows the time course of the cumulative methane production (expressed as mL STP CH_4/g COD_{added}) with digestion time for the five experimental series conducted and discussed above. Experimental methane yield values of 194±1, 188±1, 161±1, 142±10, and 124±9 mL STP CH_4/g COD_{added} were obtained for the substrates 0% LF, 25% LF, 50% LF, 75% LF, and 100% LF, respectively. Therefore,

an increase in the LF content in the mixture brought about a decrease in the methane yield. In addition, the co-digestion of OFMSW and LF of DWAS did not improve the experimental methane yield compared to the anaerobic digestion of OFMSW alone.

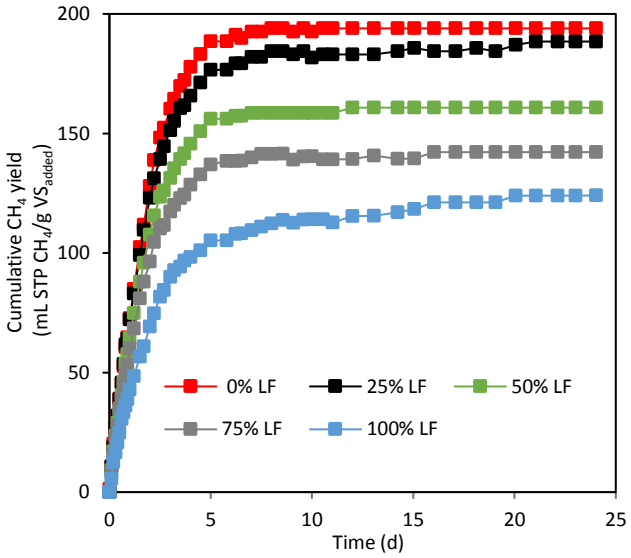

Fig. 6.1.3. Time-course of cumulative methane yield for different OFMSW to LF ratios.

The theoretical methane yield of the mixtures 25% LF, 50% LF and 75% LF calculated from the yield of mono-digestion data were found to be 176, 159 and 142 mL STP CH_4/g COD_{added}, respectively. By comparing these theoretical values with the experimental ones, only the mixture 25% LF showed a low synergistic effect, with a 6% increase in the experimental methane yield value compared to its theoretical one. Moreover, by using ratios with more OFMSW (e.g., 25% LF), LF, a residue difficult to degrade, could be managed and output. This is known because the methane yield obtained with this ratio was very similar to that obtained by digestion of OFMSW alone.

The experimental methane yield values obtained in all cases were consistently lower than the theoretical methane yield value (350 mL STP CH_4/g COD) [23], which was also obtained experimentally using control reactors with starch as a substrate. This finding agrees with data reported in the literature, which indicate that the experimental methane yield achieved in an anaerobic reactor is always lower than the theoretical one because part of the organic matter is inaccessible to microorganisms owing to the bonding among particles or to the presence of rigid structures. In addition, some organic compounds are difficult to biodegrade anaerobically, and part of the resources from the substrate is used for cell growth and maintenance.

The following efficiencies were obtained by comparing the experimental methane production obtained in this work with the above mentioned theoretical value

(350 mL CH_4/g COD): 55% for 0% LF, 54% for 25% LF, 46% for 50% LF, 41% for 75% LF, and 35% for 100% LF. The highest biomethanation efficiencies were achieved for the substrates with the highest percentages of OFMSW (0% LF and 25% LF), while the lowest efficiency was found for the substrates with higher percentages of LF. The lowest efficiency occurred with 100% LF. This is because the OFMSW usually contains high concentrations of organic matter, such as carbohydrates, lipids, and proteins, which are easily degradable by the anaerobic microorganisms, resulting in a greater methane-production potential. In contrast, the LF of DWAS is composed of alkenes, oxygen- and nitrogen-bearing aromatics, and phenolic compounds (Table 6.1.2), which are more difficult to degrade through anaerobic digestion, resulting in lower methane yields [15,40,41]. The above-mentioned compounds and other organic acids (e.g., propionic, butyric, valeric, phenylacetic) are products resulting from the hydrolytic stage of sludge decomposition, as well as from dehydration, decarboxylation, condensation, polymerization, and aromatization reactions [40].

None of the studies in the literature describe the anaerobic co-digestion of OFMSW and liquid fraction from HTC of DWAS, although there are several studies of anaerobic co-digestion of OFMSW with other substrates such as cow and pig manure, slaughterhouse wastewater, and wastes with high fat content [42-44]. Cabbai et al. [42] observed an increase in methane production of 18% and 47% in the co-digestion mixtures of source selected OFMSW (from canteens and restaurants) and waste activated sludge (WAS) at ratios of 0.23 g VS_{OFMSW}/g VS_{WAS} and 2.09 g VS_{OFMSW}/g VS_{WAS}, respectively, compared with the anaerobic mono-digestion of WAS. This was attributed to the high content of easily biodegradable carbohydrates and the appropriate ISR selected (2). In addition, Martín-Gonzalez et al. [44] achieved an increase in biogas production from 0.38 to 0.55 L/g VS_{feed} when the OFMSW was co-digested in 5 L continuous reactor with high fat, oil and grease content waste (FOGW) at mixtures of 1:7 (g VS_{OFMSW} :g VS_{FOGW}), compared to the single digestion of OFMSW.

The methane yield obtained for 100% LF in the present study was very similar to that reported by Danso-Boateng et al. [50] in the anaerobic digestion of the LF of primary sludge carbonized at 200 ºC. However, Fernández-Cegrí et al. [45] reported a methane yield of 250 mL CH_4/g COD_{added} in the anaerobic digestion of sunflower oil cake after a hydrothermal treatment at 200 ºC, giving a methane yield higher than that obtained in the present study.

Taking into account the shape of the curves of methane production with time (Fig. 6.1.3) a first-order kinetic model was used to analyze the performance of the anaerobic co-digestion of OFMSW and LF of DWAS:

$$G = G_{max} \cdot [1 - exp(-k \cdot t)] \quad \text{Eq. 6.1.2}$$

Where G is the cumulative specific methane production (mL STP CH_4/g COD_{added}), G_{max} is the ultimate methane production (mL STP CH_4/g COD_{added}), k is the specific rate constant (d^{-1}), and t is the digestion time (d). This kinetic model is normally applied to assess the kinetics of batch anaerobic digestion of different types of easily biodegradable substrates [46].

Table 6.1.4 summarizes the kinetic parameters obtained from Eq. (6.1.2) for the different co-digestion mixtures and for the substrates alone. Deviations between the experimental G_{max} values (Fig. 6.1.3) and the theoretical values (Table 6.1.4) were lower than 1% for all the cases studied, except for 100% LF, which had a 5% deviation. Therefore, the low values of the standard deviations and the high determination coefficient values prove an appropriate fit of the experimental results to the proposed model. The value of the kinetic constant for 0% LF and 25% LF was identical (0.52 d^{-1}), while for 50% LF and 75% LF, the value increased slightly to 0.54 and 0.56 d^{-1}, respectively. This demonstrates that the process kinetics did not significantly vary at increasing concentrations of LF of DWAS. The k value diminished 15% for 100% LF compared with that obtained for 0% LF and 25% LF which is primarily due to its high content of aromatic and phenolic compounds (Table 6.1.2).

Table 6.1.4. Kinetic parameters obtained from the first-order kinetic model in the batch anaerobic co-digestion experiments.

Experiment	Gmax (mL CH_4/g COD_{added})	k (d^{-1})	R^2	S.E.E.
0% LF	196±0	0.52±0.01	0.996	2.951
25% LF	186±1	0.52±0.01	0.998	2.281
50% LF	161±1	0.54±0.01	0.998	2.278
75% LF	141±0	0.56±0.01	0.999	1.995
100% LF	118±1	0.44±0.01	0.995	2.721

R^2: coefficient of determination; S.E.E.: Standard error of estimate.

The kinetic constant values obtained for 0% LF and different mixtures of OFMSW-LF were higher than those obtained for mechanically selected OFMSW, which had values ranging between 0.37 and 0.43 d^{-1} [47]. These kinetic constant values were also much

higher than those reported for batch anaerobic digestion of secondary sewage sludge alone (0.22 d^{-1}) [38].

CH_4 and CO_2 composition in the biogas during the anaerobic co-digestion of OFMSW and LF of DWAS

The composition of CH_4 and CO_2 in the biogas and their variation over time, were analyzed using gas chromatography, which allowed for comparison of these values with the corresponding values reported in the literature. The typical composition of the biogas obtained during anaerobic digestion of OFMSW comprised CH_4 (50–70%), CO_2 (30-50%), trace gases such as H_2 (0–2%), H_2S (0–8%), and NH_3 (0–1%) [10].

Fig. 6.1.4 a shows the evolution of methane percentages in the biogas during the anaerobic co-digestion of OFMSW and LF of DWAS. The trend in the variation of methane content with time was very similar for all the mixtures assayed. In all cases, the increase in the proportion of methane was significantly pronounced and rapid. In the first 5–7 d, values around 52–55% were achieved, and at the end of the experiments concentrations higher than 60% were observed, which is within the normal percentage range of production by an anaerobic digestion process at equilibrium [10]. This same trend was also observed in the anaerobic digestion of other organic wastes under different operative conditions [48].

Fig. 6.1.4 b shows the variation of the CO_2 content in the biogas with digestion time for all the anaerobic co-digestion mixtures. The trend in the evolution of CO_2 was very similar for all the mixtures and for the two substrates alone. The increase in the CO_2 content in the biogas with time was not as rapid as the increase in CH_4 content. In addition, a higher fraction of CO_2 was observed for 0% LF, while the percentage of CO_2 decreased with increasing amounts of LF. The lowest CO_2 values were consistently obtained for 100% LF. The substrates 0% LF and 25% LF achieved almost the maximum CO_2 percentages (30–35%) after 9–10 d of digestion, while the other substrates (50% LF, 75% LF, and 100% LF) reached the maximum CO_2 levels, typical of an anaerobic process at equilibrium, only at the end of the digestion time.

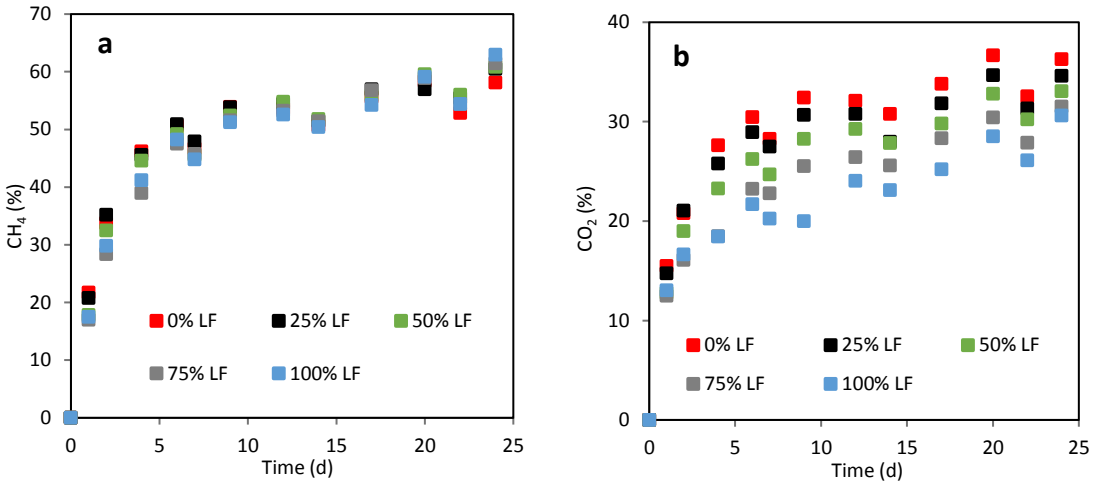

Fig. 6.1.4. Time-course of methane (a) and carbon dioxide (b) percentages for different OFMSW to LF ratios.

6.1.4. Conclusions

The pre-treatment of the OFMSW after grinding and sieving (20 mm diameter) produced a higher methane yield from batch anaerobic digestion than that from untreated OFMSW. The experimental data (methane production and time) fit adequately to the modified Gompertz model, which predicted process performance. The maximum methane production rate, μ for *ground+sieved* OFMSW was 2.4 times higher than the value for untreated OFMSW.

The anaerobic co-digestion of different mixtures of OFMSW and the LF of DWAS did not improve the methane yield with respect to the anaerobic digestion of OFMSW alone, and no synergistic effects were observed. However, a mixture of 25% LF provided a similar methane yield to that obtained with 0% LF; thereby providing an alternative by which a waste that is very difficult to biodegrade, such as LF, could be managed and treated by co-digestion with OFMSW. A first-order kinetic model demonstrated that the kinetic constant is virtually independent of the percentage of LF as co-substrate, and decreased slightly for 100% LF alone.

The percentages of CH_4 and CO_2 in the biogas for the above-mentioned mixtures increased significantly and rapidly with time, reaching 55–60% and 30–35%, respectively.

6.1.5. References

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6.2

Anaerobic co-digestion of the organic fraction of municipal solid waste and the liquid fraction from the hydrothermal carbonization of industrial sewage sludge under thermophilic conditions

J.A. Villamil, A.F. Mohedano, J.J. Rodriguez, R. Borja, M.A. De la Rubia, Anaerobic co-digestion of the organic fraction of municipal solid waste and the liquid fraction from the hydrothermal carbonization of industrial sewage sludge under thermophilic conditions, Front. Sustain. Food Syst. 2:17 (2018) 1–7

Abstract

The anaerobic thermophilic co-digestion of mixtures of the organic fraction of municipal solid waste (OFMSW) and the liquid fraction from the hydrothermal carbonization (LF) of dewatered waste activated sludge was studied. Mixtures with a low OFMSW to LF ratio (50, 75 and 100% LF) exhibited accumulation of volatile fatty acids (VFA) as well as low degradation of organic matter and methane production. However, the mixture containing 25% LF performed quite well in terms of methane production: (179±3) mL STP CH_4/g COD_{added}, which was only slightly lower than the value obtained with 0% LF. The experimental results fitted the modified Gompertz model reasonably well and the maximum methane production rate for the mixture containing 25% LF (11.96 mL CH_4/g COD·d) was 29.3% higher than that obtained with the substrate with 0% LF. Therefore, centralized co-digestion of OFMSW in mixtures with 25% LF seemingly provides an effective method for valorizing the latter substrate.

6.2.1. Introduction

Thermochemical conversion processes are typically used to convert biomass into valuable products or biofuel. Specifically, hydrothermal carbonization (HTC) at 180–260 ºC under auto-generated pressure is a promising method for converting wet biomass [1,2]. Thus, HTC converts biomass into a valuable solid product called "hydrochar" in addition to a liquid fraction (LF) and a gas stream. HTC is especially suitable for biomass waste with a high moisture content such as sewage sludge produced in wastewater treatment plants (WWTP). Because this hydrochar possesses a higher heating value (ca. 22 MJ/kg), hydrothermal conversion of sewage sludge can be an effective, inexpensive choice for its management. Also, the resulting liquid fraction (LF) has a total chemical oxygen demand (COD) of nearly 100 g O_2/L [3], which justifies its valorization to recover organic matter up to 15% of all initial carbon [4].

The liquid fraction obtained by HTC of organic waste is used as feedstock for chemical production or recycled in consecutive HTC runs to improve carbon yield [5,6]; also, it can be subjected to wet air oxidation, aerobic degradation or anaerobic digestion [7–9]. However, the presence of recalcitrant compounds formed during the thermal treatment (furfural, phenols, furans, pyrazines and pyridines) detracts from methane yields in anaerobic digestion [3,7,10,11].

One of the advantages of co-digestion processes (viz., the simultaneous digestion of two or more substrates) is that it dilutes toxic compounds [12]. This makes co-digestion of LF with another organic waste a suitable choice for LF valorization. Anaerobic co-digestion is by now a well-established technology [13–15], and co-digestion of sewage sludge (SS) and the organic fraction of municipal solid waste (OFMSW) is most widely explored combination [16].

OFMSW anaerobic digestion is a widely used green method and an advantageous alternative to traditional management choices for organic solid wastes (e.g., landfill refuse) with reduced methane emission and energy production [17]. However, the usual practice of performing OFMSW digestion under mesophilic conditions necessitates revision and improvement. In fact, processing OFMSW at a thermophilic temperature rather than at mesophilic levels affords high waste loads, increased biogas production and effective destruction of pathogenic microorganisms, which leads to improved hygienization of solid waste material for use on land [16]. Also, using a digestion co-substrate can increase biogas production or even methane yield in traditional anaerobic digestion processes for organic wastes [18]. LF can be an useful co-substrate for this purpose on account of its high organic matter content [3]. In addition, anaerobic co-digestion could aid the process by balancing the C:N ratio and increasing buffering capacity [19]. However, optimizing co-digestion requires using the best possible blend to exploit synergistic and complementary effects, as well as to maximize methane production while avoiding inhibition [20]. In this work, we explored the batchwise anaerobic co-digestion under thermophilic conditions of mixtures of the liquid fraction from the hydrothermal carbonization of dewatered waste activated sludge and the organic fraction of municipal solid waste in variable ratios with a view to improving methane yields in relation to the processing of either substrate alone. Process performance was assessed in terms of various parameters including methane yield.

6.2.2. Materials and methods

Inoculum source

The starting anaerobic digestate was collected from a full-scale mesophilic reactor processing OFMSW from a municipal solid waste treatment plant (MSWTP) in the Spanish region of Madrid. The mixed anaerobic culture used as thermophilic inoculum was obtained by directly switching from mesophilic (35 ºC) to thermophilic conditions

(55 ºC) according to De la Rubia et al. [21]. The main properties of the inoculum were as follows: pH 8.2±0.1, total solids (97.9±0.4) g TS/kg; volatile solids (45.3±0.5) g VS/kg; and total chemical oxygen demand (36.6±3.3) g O_2/L.

Substrates

a. Co-substrate 1.

OFMSW was collected from the waste reception area of the aforementioned MSWTP. Although the solid waste delivered at the treatment plant is source segregated at household level, it still contains considerable amounts of plastic, paper, cardboard, metal and glass. An amount of approximately 100 kg of OFMSW was sorted by hand and its non-OFMSW portion removed prior to grinding in a mill. Finally, the shredded organic waste was sieved to a final particle size smaller than 0.02 m for use. This substrate contained (24.5±2.9)% C, (1.6±0.5)% H, (1.9±0.2)% N and (0.1±0.05)% S, and its main characteristics were as follows: (437±9) g TS/kg; (283±3) g VS/kg and total COD (1157±10) mg O_2/g TS.

b. Co-substrate 2.

LF was obtained by hydrothermal carbonization of dewatered waste activated sludge, with an 85% moisture content, collected from a full-scale membrane bioreactor processing industrial wastewater from a cosmetics factory. The substrate was stored at -20 ºC until use. HTC was performed by using 1.5 kg of dewatered waste activated sludge in an electrically heated 4 L ZipperClave® pressure vessel at 208 ºC. The operating temperature was reached at a heating rate of 3 ºC/min and held for 1 h. The reaction was stopped by cooling with an internal heat exchanger using tap water. The slurry obtained (470 g of wet hydrochar and 530 g of LF for each kg of wet material treated) was centrifuged at 3500 rpm for 1 h, filtered (Albet FV-C, 0.45 µm) and stored at 4 ºC until anaerobic digestion. HTC allowed obtaining a dry basis hydrochar with 40.1% yield, 21.6 MJ/kg higher heating value and the following elemental composition: 43.1% C, 5.8% H, 0.2% S and 4.6% N.

The composition and main properties of the LF were as follows, each given as the average of three determinations±standard deviation: pH 5.1±0.1, (94.6±2.0) g/L soluble COD (SCOD), (42.6±1.7) g TOC/L, (55.7±0.5) g TS/L, (46.2±0.5) g VS/L and (8.7±0.1) g/L total Kjeldahl nitrogen (TKN). This co-substrate was analyzed by GC/MS [22], which

allowed the identification of nitrogen-containing species (pyrazines and aromatic amines) and oxygen-containing aromatic compounds (phenols and furans).

Experimental set-up

Anaerobic co-digestion runs were done batchwise in 120 mL glass serum vials that were kept under thermophilic conditions (55±1 ºC) in a Julabo thermostatic water bath shaker operating at 80 rpm. The operational sequence used in each run comprised 9 fed reactors and 3 controls. The fed reactors were initially loaded with the required amounts of the two co-substrates, six being sacrificed and removed each day initially and then weekly until the end of the experiment, in order to assess changes in chemical parameters at different times during the anaerobic digestion process. The other three reactors were used for biogas analysis (volume and composition) only. Methane production through biomass decay, and residual substrate potentially present in the inoculum, as determined in the controls, were subtracted from the experimental values. All experiments were allowed to develop until no significant gas production was observed and biodegradation was thus essentially complete as in the controls with starch (ca. 350 mL CH_4/g COD_{added}), which took approximately 55 days.

Batch co-digestion runs used an inoculum concentration of 15 g VS/L and an ISR value of 2.0, on a COD basis, as widely recommended [3,23–25]. The co-substrates were used in different ratios, namely: 0, 25, 50, 75 and 100% LF, all on a COD basis. A basal medium of macro- and micronutrients was prepared according to Villamil et al. [3]. Also, a 10% (v/v) solution of 50 g $NaHCO_3$/L was used to obtain a TA value of 3.4 g $CaCO_3$/L at the beginning of the reaction (time zero). Finally, the reactors were filled up to 60 mL with dionised water, the reaction medium being flushed with N_2 for 3 min in order to ensure anaerobic conditions and the vials sealed with rubber stoppers and metal crimps.

Analytical methods

Dry matter, TS and VS were determined according to standard methods 2540B and 2540E [26], and total COD according to Raposo et al. [27]. pH was measured with a Crison 20 Basic pH meter. Partial alkalinity (PA) and total alkalinity (TA) were determined by titration to pH 5.75 and 4.3, respectively [28]. Intermediate alkalinity (IA), defined as the difference between TA and PA, and SCOD were assessed by closed digestion and with standard colorimetric method 5220D, respectively [26]. TKN was measured as described elsewhere [26]; total ammonia nitrogen (TAN) by distillation and titration according to

standard method 4500E [59]; and free ammonia nitrogen (FAN) according to Hansen et al. [29]. The elemental composition of the inoculum and co-substrates was determined with a LECO CHNS-932 CHNS analyzer. The concentrations of individual volatile fatty acids (VFA) from acetic to heptanoic, iso forms included, were determined on a Varian 430 gas chromatograph equipped with a flame ionization detector (FID) and a capillary column filled with Nukol (polyethylene glycol modified by nitroterephthalic acid) according to De la Rubia et al. [22]. Biogas and methane production expressed at standard temperature (273 K) and pressure (1 bar) were measured once daily over the first 3 days and 12 more times through the incubation period. H_2, CO_2 and CH_4 were determined on a Thermo Scientific Trace 1300 gas chromatograph equipped with a thermal conductivity detector (TCD) and a 8 ft × 1/8 in SS column packed with HayeSep Q 80/100 mesh [60].

6.2.3. Results and discusion

pH, alkalinity and ammonia nitrogen

The pH values at the end of the co-digestion process were 8.1–8.2, and hence very similar in all runs and typical for anaerobic digestion under thermophilic conditions [21,30]. These values are suitable for growing methanogenic *Archaea*, which are extremely sensitive to pH changes [31].

Table 6.2.1 shows the final total alkalinity (TA), partial alkalinity (PA) and intermediate to total alkalinity (IA/TA) ratios, as well as the final TAN and FAN value. As can be seen, TA ranged from 10.3 to 11.3 g $CaCO_3$/L and was thus high enough to ensure acceptable buffering capacity. In fact, an IA/TA ratio lower than 0.3 ensures efficient operation of anaerobic processes, so the buffering capacity of the medium was adequate. Hydrolysis reactions are favored by thermophilic conditions, which boost protein degradation and ammonia nitrogen production as a result [21]. Nitrogen is essential for protein synthesis and primarily a nutrient for microorganisms in anaerobic digestion; on the other hand, total ammonia nitrogen (TAN) has some buffering effect on anaerobic digestion systems. Nitrogen in the form of ammonium ion (NH_4^+) can react with bicarbonate ion to form NH_4HCO_3. However, ammonia (NH_3) has been suggested to be the active component inhibiting microbial methanogenesis [32]. The free ammonia level depends mainly on three parameters, namely: TAN concentration, temperature and pH [29]. An increase in pH results in a marked concentration increase in free ammonia (e.g., 8 times for a pH rise from 7 to 8) [33]. As can be seen, TAN ranged from 2044 to 2212 mg/L and FAN from

709 to 791 mg/L. According to Chen et al. [34], TAN concentrations over the range 1500-7000 mg/L, which is very broad and encompasses a variety of substrates and conditions, can inhibit methanogenesis. Our TAN values fell slightly above the lower limit of inhibition but were very far from the upper limit. As consequence, slight inhibition of methanogenic activity by ammonia nitrogen might have occurred. However, our FAN values were lower than the limit reported by Hansen et al. [29] for inhibition in the anaerobic degradation of swine manure in batch cultures (1.1 g/L). As can be seen from Table 6.2.1, FAN increased with decreasing OFMSW/LF ratio, probably due to the intimate relationship between the pH of the medium, higher than 8 in all runs, and the proportion of ammonia/ammonium as a function of temperature.

Table 6.2.1. Total alkalinity (TA), partial alkalinity (PA), intermediate to total alkalinity (IA/TA) ratio, total ammonia nitrogen (TAN) and free ammonia (FAN) at the end of the experiments.

Substrate composition (% LF)	**TA (mg $CaCO_3$/L)**	**PA**	**IA/TA**	**TAN (mg/L)**	**FAN (mg/L)**
0	10343±115	7775±39	0.25	2156±15	709±10
25	11042±228	8246±237	0.25	2163±10	745±7
50	11299±69	8191±56	0.28	2198±8	757±8
75	11299±76	8038±6	0.29	2212±17	775±12
100	10660±76	7473±28	0.30	2044±20	791±12

Volatile fatty acids and soluble COD

VFA evolution is central to the development of anaerobic digestion. Fig. 6.2.1 shows the VFA profile obtained at the end of the experiments with the different OFMSW/LF ratios studied. As can be seen, accumulation of VFA such as propionic, isobutyric, isovaleric and valeric increased with increasing proportion of LF. The presence of these acids has a negative effect on methane production; in fact, the acids are difficult to degrade (particularly propionic), so their accumulation can lead to inhibition of methanogenic *Archaea*. De la Rubia et al. [21] reported that thermophilic conditions tend to generate high concentrations of VFA in the medium, which coincides with the results obtained experimentally. As can be seen in Fig. 6.2.1, using a proportion of LF higher than 50% led to a propionic acid concentration exceeding 850 mg/L. Wang et al. [35] found that propionic acid concentration of 900 mg/L led to considerable anaerobic digestion inhibition. This propionic acid concentration was also found to have inhibitory effects by

Qiao et al. [36] in processing the supernatant of hydrothermally treated municipal sludge in an upflow anaerobic sludge blanket reactor. In fact, conditions with of LF higher than 50% reached lower methane yields, as more forward will be checked.

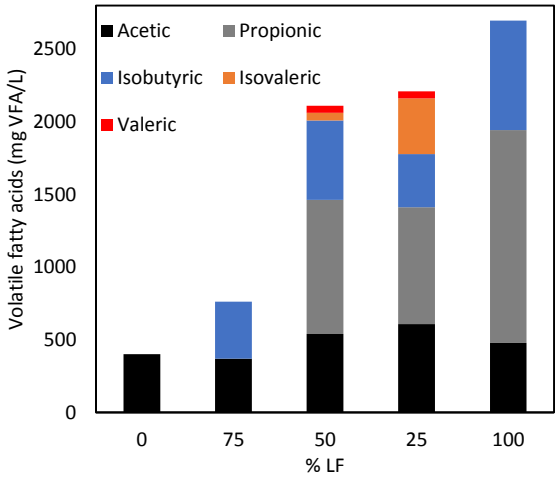

Fig. 6.2.1. VFA profile (expressed as mg/L) at the end of the experiments with substrates of variable composition.

Table 6.2.2 shows the SCOD values at the end of the experiments. As can be seen, there were two clear-cut trends. Thus, the mixtures with the highest proportions of OFMSW (0% and 25% LF) exhibited the lowest SCOD values. Since the initial COD concentration was identical in all trials, these runs were those providing the highest methane yields. On the other hand, the mixtures with high proportions of LF (50, 75 and 100% LF) led to high SCOD levels (i.e., to less efficient degradation of organic matter and hence to decreased methane generation). As expected, the runs with high SCOD values also led to high VFA concentrations. VFA, in mg COD/L, accounted for a substantial fraction of SCOD in the samples containing more than 50% LF, probably as a result of its partially inhibiting the methanogenic population.

Table 6.2.2. SCOD and VFA values (as mg SCOD/L) at the end of the experiments.

Substrate composition (% LF)	**SCOD (mg O_2/L)**	**VFA (mg COD/L)**	**VFA/SCOD (%)**
0	2918±8	430±1	14.7
25	4149±31	892±7	21.5
50	7176±9	2259±9	31.5
75	7664±9	2317±13	30.2
100	6338±23	3776±15	59.6

Methane production and kinetics

Fig. 6.2.2 shows the time course of methane yield, in mL STP CH_4/g COD_{added}, in the anaerobic co-digestion runs. Methane production at the end of the runs ranged from (51±1) to (209±1) mL STP CH_4/g COD_{added} for the individual substrates (LF and OFMSW), respectively, while methane yields relative to the theoretical value (350 mL CH_4/g COD) were 14.6 and 59.6%. The maximum theoretical methane production was never reached because some organic matter is usually inaccessible, some compounds are difficult to degradable and a fraction of the substrate is used for cell growth and maintenance [37]. The highest yields were obtained in the runs involving the highest proportions of OFMSW (0% and 25% LF); on the other hand, methane production decreased with increasing LF content in the mixture. The OFMSW substrate contained large amounts of organic matter of easy degradation by anaerobic microorganisms and thus had a high potential for biogas production. By contrast, the LF substrate contained recalcitrant compounds (viz., nitrogen-containing species such as pyrazines and aromatic amines, and oxygen-containing aromatic compounds such as phenols and furans) and such compounds were difficult to degrade and led to lower methane yields [10].

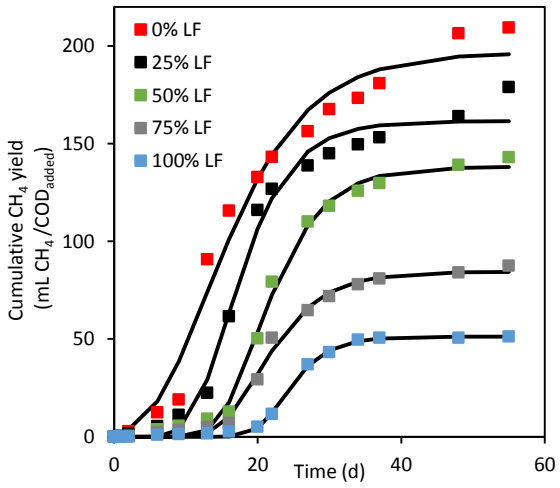

Fig. 6.2.2. Time-course of methane production in the experiments. Symbols represent experimental values and the solid lines predicted values.

A comparison of the methane yields obtained in the runs with 0% and 25% LF under thermophilic conditions ((209±1) and (179±3) mL STP CH_4/g COD_{added}, respectively) with those obtained under mesophilic conditions ((194±1) and (188±1) mL STP CH_4/g COD_{added}, respectively) [22], revealed an increase by 7.7% with 0% LF under thermophilic conditions, but similar yields with 25% LF.

Cabbai et al. [38] studied the anaerobic co-digestion of OFMSW and sewage sludge obtaining a similar trend in methane yield by reducing the proportion of OFMSW in the starting mixture. Also, our yields were lower than those reported by Qiao et al. [39] for the anaerobic digestion of the liquid fraction from the HTC of mixed (primary and secondary) sewage sludge (257 mL CH_4 /g COD). However, these authors performed HTC at 120-190 ºC, which is much lower than the temperature used here (208 ºC). In any case, Wirth et al. [40] obtained similar methane yields (120–180 mL STP CH_4/g COD_{added}) by using the liquid fraction from HTC of digested sewage sludge as their sole substrate in the continuous feed mode.

Methane yields were fitted to the modified Gompertz model. The model uses a sigmoidal function similar to a time series where the growth rate is very low at the beginning and end [41]. This equation is probably one of the best functions for predicting biogas production in batchwise anaerobic digestion processes; also, it has been calibrated and tested with large amounts of experimental data by a number of researchers [41–43].

In the modified Gompertz model, cumulative methane production is related to digestion time by the following equation:

$$G(t) = G_{max} - exp\left[-exp\left(\frac{\mu}{G_{max}} \cdot (\lambda - t) \cdot e^1 + 1\right)\right] \quad \text{Eq. 6.2.1}$$

where $G(t)$ is the cumulative methane production at time t (mL CH_4/g COD_{added}), G_{max} the maximum methane production or methane yield potential (mL CH_4/g COD_{added}), μ the maximum methane production rate (mL CH_4/g COD_{added}·d), λ the lag time (d), t the digestion time (d) at which methane production is calculated and e denotes exp (1) =2.7183. Parameters G_{max}, μ and λ for each run were calculated by using the non-linear regression routine in the software SigmaPlot 11.0.

Table 6.2.3 shows the values of the model parameters for each run as obtained with the modified Gompertz model. As can be seen, the model fitted the experimental data quite acceptably, with low standard errors of estimate (SEE). The differences between the experimental and calculated values of G_{max} were smaller than 5% in most cases. On the other hand, the determination coefficients exceeded 0.99 in almost all. A decrease in theoretical ultimate methane yield with increasing proportion of LF was observed. The substrate mixture containing 25% LF exhibited a smaller value than the sole OFMSW substrate. However, the ultimate methane yield was considerably lower with all other

substrate compositions, (138, 84 and 51 mL STP CH_4/g COD_{added}, respectively). The highest methane production rate was that for the mixture 25% LF: 11.96 mL CH_4/g COD·d, which was 29.3% higher than that for the 0% LF. Also, increasing the proportion of OFMSW decreased the maximum methane production rate from 11.96 to 5.33 mL CH_4/g COD·d. In addition, the lag time increased considerably (from 4.9 to 19.7 days) as the proportion of LF in the mixture was increased as a result of the presence in this substrate of complex organic acids and other inhibitory substances that are difficult to degrade anaerobically.

Table 6.2.3. Parameters[a] of the modified Gompertz model for the individual substrates and the co-substrate mixtures.

Substrate composition (% LF)	G_{max} **(mL CH_4/g COD)**	μ **(mL CH_4/g COD·d)**	λ **(d)**	R^2	**Error[b] (%)**	**SEE[c]**
0	197±7	9.25±1.04	4.9±1.1	0.982	5.8	11.52
25	162±4	11.96±1.38	10.7±0.8	0.989	9.4	8.02
50	138±2	9.87±0.72	14.6±0.5	0.996	3.5	4.25
75	84±2	6.12±0.51	14.7±0.6	0.995	3.8	2.94
100	51±2	5.33±0.29	19.7±0.2	0.998	0.3	1.15

[a] *p* values were less than 0.0001 for all parameters
[b] Error $[(G_{\text{max experimental}} - G_{\text{max model}})/G_{\text{max experimental}}]$
[c] SEE: Standard error of estimate

6.2.4. Conclusions

Thermophilic anaerobic co-digestion of OFMSW and LF mixtures failed to increase methane yield with respect to the anaerobic digestion of OFMSW alone; also, no synergistic effect was observed. However, a mixture containing 25% LF provided methane yields very close to those obtained with 0% LF. This substrate combination provides an alternative management method for this waste (LF): co-digestion with OFMSW. Methane production decreased with increasing content of LF in the mixtures because this substrate contains recalcitrant compounds that are difficult to degrade by methanogenic microorganisms. However, anaerobic tests with mixtures containing more than 25% LF inhibited methanogenesis through increasing accumulation of VFA as the proportion of this substrate in the mixture was increased. The time course of methane production fitted the modified Gompertz model quite well.

6.2.5. References

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Conclusions/Conclusiones

Conclusions

The results presented in this work support the following conclusions:

Production of inexpensive activated carbons from dewatered waste activated sludge by hydrothermal carbonization and activation processes

1. The hydrothermal carbonization can be a viable option for the valorization of dewatered waste activated sludge (DWAS) by the production of a hydrochars with high energy density and similar characteristics to bituminous coal (higher heating value in the range of 19.1-22.3 MJ/kg). Hydrochars showed volatile matter content lower than 75% and exceed the maximum nitrogen content (<3%), which fails to comply with the fuel quality classes and specifications of graded densified solid biofuels produced from thermally treated biomass. Thus, this renewable solid fuel could be blended with other biomass residues to improve the combustion behavior and reduce NO_x emissions.
2. Hydrochar could be used as a precursor of activated carbons with a number of oxygenated functional groups that conferred unique textural and surface properties. HTC of DWAS followed by air activation produced activated carbons with moderate BET areas (100 m^2/g at best). Activated carbons with relatively large surface area (410-1030 m^2/g) and different porous structure (important contribution of meso and microporosity) were obtained by chemical activation using hydrochar as feedstock, which could have potential application as absorbents or catalytic supports.

Valorization of the liquid fraction from hydrothermally treated dewatered waste activated sludge by anaerobic digestion

3. The liquid fraction from HTC of dewatered waste activated sludge was characterised by high COD (95.5 g/L) and TKN (8.7 g N/L) content, and can be a potential substrate for an anaerobic digestion treatment under mesophilic conditions. In that respect, the inoculum source, the inoculum concentration and the inoculum to substrate ratio must be adequately selected for proper operation of the process and successful valorization. High inoculum concentration (25 g COD/L) and/or low ISR (≤0.5) affected negatively the ultimate methane yield through methanogenesis inhibition, due to the high ammonia nitrogen and VFA concentration released. According to the results, working with an ISR≥1 is recommended.

4. The inoculum origin and its structure were determinant in the treatment of the LF of the dewatered waste activated sludge hydrothermally treated by mesophilic anaerobic digestion. Although high COD removal efficiencies were achieved for each inocula studied (granular biomass from industrial reactors treating brewery and sugar beet wastewaters and a flocculent biomass from a full-scale digester of municipal sewage sludge), the methane yields were very dependent of the inoculum source. Among the three inocula tested, brewery granular biomass appeared to be the best in terms of methane production working at high inoculum concentration (25 g COD/L), although the significantly lowest values of the kinetic constant reveal a slow organic matter degradation.

Anaerobic co-digestion of the liquid fraction from hydrothermally treated waste activated sludge with primary sewage sludge

5. The co-digestion of the LF of dewatered waste activated sludge with primary sewage sludge can provide a feasible way of integrating the HTC of dewatered waste activated sludge in a wastewater treatment plant. Operating in batch mode and for the both inocula used (a flocculent sludge from a mesophilic digester of a municipal wastewater treatment and a granular one from a brewery wastewater treatment plant), the increase in the LF to PSS ratio decreased the methane production, due to the presence of inhibitory nitrogen-containing aromatic compounds detected in the process water.
6. The granular inoculum provided better results in terms of ultimate methane yield than the flocculent one. The highest methane yields were found for the experiments with 25% LF (1.76 and 1.30-fold increase with respect to the bare LF, with the flocculent and granular inoculum, respectively). With that mixture, SCOD removals around 85–90% were obtained, with no residual VFAs detected.
7. The anaerobic co-digestion of the LF of dewatered waste activated sludge with primary sewage sludge was optimized by performing semi-continuous experiments with different feed mixture compositions, organic loading rates, and temperature regimes. Under thermophilic conditions, the co-digestion showed progressive inhibition evidenced by indole accumulation. Also, high concentrations of VFA and NH_3 and low methane yield were observed.
8. The anaerobic co-digestion of LF and PSS under mesophilic regime, working at low OLR (1.5 g COD/L·d) led to a 1.15 times higher methane yield with the 10% LF mixture than with the control treatment (100% primary sewage sludge).

COD removal was at least 53% and irrespective of the operating conditions used. Meanwhile, TAN, alkalinity and VFA fell within the ranges for stable operation of the digester. Therefore, the overall process provided a positive energetic balance (hydrochar+biogas) around 2.0 times higher than with control treatment and 4.4 times higher than with conventional anaerobic digestion of mixed sludge.

Anaerobic co-digestion of the liquid fraction from hydrothermal carbonization of dewatered waste activated sludge and the organic fraction of municipal solid waste

9. The anaerobic digestion of pretreated OFMSW after grinding and sieving (20 mm) produced a higher methane yield under mesophilic conditions in batch mode than that from untreated OFMSW. The methane production fitted adequately to the modified Gompertz model. The maximum methane production rate was 2.4 times higher than the value for untreated OFMSW.
10. The anaerobic co-digestion of different mixtures of OFMSW and the LF of DWAS did not improve the methane yield compared to the anaerobic digestion of OFMSW alone, and no synergistic effects were observed. However, the mixture with 25% LF provided a similar methane yield to that obtained with OFMSW as sole substrate. A first order equation fitted adequately the experimental result of methane production. The kinetic constant was virtually independent of the percentage of LF as co-substrate (0.52–0.56 d^{-1}), and decreased slightly for the experiment performed with LF as sole substrate LF (0.44 d^{-1}). The percentages of CH_4 and CO_2 in the biogas for the mixture with 25% LF reached values of 55–60% and 30-35%, respectively.
11. The thermophilic anaerobic co-digestion of OFMSW and LF mixtures failed to increase methane yield with respect to the anaerobic digestion of OFMSW alone; also, no synergistic effect was observed. Methane production decreased with increasing content of LF in the mixtures because this substrate contains recalcitrant compounds that are difficult to degrade by methanogenic microorganisms under thermophilic conditions. The mixture containing 25% LF provided methane yields very close to those obtained with 0% LF. However, anaerobic tests with mixtures containing more than 25% LF inhibited methanogenesis through increasing accumulation of VFA. The time course of methane production adequately fitted the modified Gompertz model.

Conclusiones

Los resultados presentados en esta memoria permiten establecer las siguientes conclusiones:

Producción económica de carbones activos de bajo coste a partir de fango secundario deshidratado mediante carbonización hidrotermal y procesos de activación

1. La carbonización hidrotermal de fango secundario deshidratado resulta una opción viable para la producción de hidrochar con elevada densidad energética y similares características que los carbones sub-bituminosos (poder calorífico superior en el intervalo de 19,1-22,3 MJ/kg). Los hidrochars alcanzan un contenido en materia volátil inferior al 75% y exceden el contenido máximo de nitrógeno (<3%), por lo que imcumple las especificaciones de los biocarburantes sólidos producidos a partir de biomasa tratada térmicamente. Por ello, el hidrochar podría mezclarse con otros residuos biomásicos para mejorar sus características y reducir las emisiones de NOx.
2. Los hidrochars pueden usarse como precursores de carbones activados con grupos oxigenados superficiales que les confieren interesantes propiedades texturales y superficiales. La carbonización hidrotermal de lodo secundario deshidratado seguida de activación por aire origina carbones activados con valores reducidos de área BET (100 m^2/g en el mejor de los casos). Sin embargo, la activación química genera carbones activos con elevadas áreas BET (410-1030 m^2/g), con una importante contribución meso y microporosa lo que permitiría su empleo como adsorbentes o soportes catalíticos.

Valorización de la fracción líquida obtenida tras el tratamiento hidrotermal de lodo secundario deshidratado mediante digestión anaerobia

3. La fracción líquida procedente de la carbonización hidrotermal de fango de depuradora deshidratado contiene elevadas concentraciones de DQO (95,5 g /L) y nitrógeno total Kjeldahl (8,7 g N/L), y por tanto es un sustrato adecuado para ser tratado mediante digestión anaerobia. Este proceso requiere de la selección de un inóculo adecuado, así como de la concentración de inóculo y la relación inóculo-sustrato a utilizar para una adecuada operación de los digestores. El empleo de elevadas concentraciones de inóculo (25 g DQO/L) y/o bajas relaciones inóculo-sustrato (≤0,5) afectaron negativamente al rendimiento en metano, al producirse inhibición de la metanogénesis, debido a las elevadas

concentraciones de AGVs y nitrógeno amoniacal producidas. Por ello, se recomienda operar con relaciones inóculo-sustrato iguales o superiores a 1.

4. El origen del inóculo y su estructura resultaron determinantes en el tratamiento de la fracción líquida de la carbonización hidrotermal de fango secundario mediante digestión anaerobia en condiciones mesofílicas. Con todos los inóculos empleados (biomasa granular obtenida de reactores anaerobios que trataban aguas residuales generadas en la producción de azúcar a partir de remolacha y de la producción de cerveza, así como biomasa floculenta obtenida del digestor anaerobio de una estación depuradora de aguas residuales urbanas) se consiguieron elevadas eficiencias de eliminación de DQO. Sin embargo, el rendimiento en metano resultó ser muy dependiente del tipo de inóculo utilizado. De los tres inóculos ensayados, la biomasa granular procedente del reactor de la industria cervecera presentó los mejores resultados en términos de producción de metano, empleando una concentración de inóculo elevada (25 g DQO/L). Sin embargo, los valores de la constante cinética obtenida para este inóculo alcanzaron valores significativamente bajos, lo que da idea de la reducida velocidad de degradación de la materia orgánica.

Codigestión anaerobia de fango primario y de la fracción líquida obtenida en la carbonización hidrotermal de fango secundario deshidratado

5. La codigestión de fango primario y de la fracción líquida obtenida en la carbonización hidrotermal de fango secundario deshidratado puede proporcionar un procedimiento viable para integrar la carbonización hidrotermal de fango secundario en una estación depuradora de aguas residuales. Operando en condiciones mesofílicas e independientemente del inóculo empleado (biomasa granular de un reactor de una industria cervecera o biomasa floculenta del digestor de una EDAR), el aumento de la relación fracción líquida a fango primario disminuyó la producción de metano, debido a la presencia de compuestos aromáticos nitrogenados detectados en el agua del proceso de carbonización.
6. El inóculo granular de la industria cervecera proporcionó mejores resultados en términos de rendimiento en metano, que el inóculo floculento. La mayor producción de metano se consiguió operando con una mezcla con un 25% de fracción líquida en base a DQO, lo que supuso un aumento del 76 y del 30% para el inóculo floculento y granular, respectivamente, respecto a emplear

únicamente fracción líquida como sustrato. Empleando dicha mezcla, la eliminación de DQO resultó alrededor del 85–90%, no detectándose presencia de AGVs residuales en la mezcla de digestión.

7. La codigestión de fango primario y de la fracción líquida obtenida en la carbonización hidrotermal de fango secundario deshidratado se optimizó mediante la realización de experimentos de larga duración en operación semicontinua, empleando diferentes mezclas de ambos sustratos, cargas orgánicas y rango de temperatura. Operando en condiciones termofílicas, la codigestión de las mezclas ensayadas originó una progresiva inhibición, que se evidenció por la acumulación de indol en el digestor, así como por la presencia de elevadas concentraciones de AGVs y amoníaco y una reducida producción de metano.
8. El rendimiento en metano de la digestión anaerobia mesofílica de fango primario (100%) a baja velocidad de carga orgánica (1,5 g DQO/L) se puede mejorar un 15% digiriendo una mezcla con el 10% de fracción líquida. Además, se alcanzan valores de eliminación de DQO del 53%. Los niveles de nitrógeno amoniacal, alcalinidad y AGVs se mantuvieron en niveles aceptables para una operación estable de un digestor anaerobio. El proceso en su conjunto proporciona un balance energético positivo (hidrochar+biogas), en torno a 4,4 veces mayor que el obtenido mediante la digestión anaerobia de mezcla de fango primario y secundario, procedimiento habitualmente empleado en las EDAR.

Codigestión anaerobia de la fracción orgánica de los residuos urbanos y de la fracción líquida obtenida en la carbonización hidrotermal de fango secundario deshidratado

9. La digestión anaerobia de la fracción orgánica de los residuos urbanos (FORU), pretratados mediante molienda y posterior tamizado, mediante experimentos en discontinuo generó una producción de metano 2,4 superior al valor obtenido para el FORU sin tratar. Los resultados de evolución de producción de metano con el tiempo se ajustaron adecuadamente al modelo de Gompertz modificado.
10. La codigestión anaerobia de la fracción orgánica de los residuos urbanos (FORU) y la fracción líquida obtenida en la carbonización de fango secundario no mejoró la producción de metano respecto a la digestión del FORU como único sustrato. Tampoco se observó un efecto sinérgico en la codigestion de las mezclas estudiadas. No obstante, se alcanzó una producción de metano para la

mezcla del 25% de fracción líquida similar a la alcanzada empleando únicamente FORU. El modelo cinético de primer orden se ajustó adecuadamente a los resultados experimentales. La constante cinética resultó independiente del porcentaje de fracción líquida en la mezcla empleada como sustrato (0,52-0,56 d^{-1}) y mostró un valor ligeramente inferior para el ensayo realizado con la fracción líquida como único sustrato (0,44 d^{-1}). El porcentaje de CH_4 y CO_2 en el biogás para el ensayo con un 25% de fracción líquida se situó en el intervalo entre 55-60% y 30-35%, respectivamente.

11. La codigestion en condiciones termofílicas de FORU con mezclas de fracción líquida obtenida en la carbonización hidrotermal de fango secundario no mejoró la producción de metano comparado con la digestión de FORU como sustrato unico. La producción de metano disminuyó al aumentar el porcentaje de fracción líquida en la mezcla debido a la presencia de compuestos aromáticos nitrogenados recalcitrantes, inhibitorios bajo condiciones termófílicas. La producción de metano empleando una mezcla con un 25% de fracción líquida resultó muy similar a la alcanzada utilizando FORU como único sustrato. Los ensayos realizados con mezclas superiores al 25% de fracción líquida se inhibieron debido a la acumulación de AGVs. Los resultados de evolución de producción de metano con el tiempo se ajustaron adecuadamente al modelo de Gompertz modificado.

Suggestion for future research directions

Suggestion for future research directions

This Ph.D. thesis provides the following insights for future research:

- The issue of hydrochar applications is an intriguing one, which could be usefully explored in further research. Hydrochar as precursor of inexpensive activated carbons with tunable surface chemistry and high oxygenated functional groups could be assessed as well as specific applications such as soil amendment, catalyst support and/or adsorbent.
- From a technical and economical point of view, further investigation into the design and simulation of the hydrothermal carbonization process is strongly recommended. Very few studies have been focused on determining the energy efficiency of the HTC process through a modeling approach and especially concerning energy integrations and heat recovery using pinch analysis. A greater focus on techno-economic analysis could produce interesting findings concern investment and operational costs saving for a large-scale HTC plant.
- As far as nutrient recovery in hydrochar is concerned, phosphorus, nitrogen, and potassium represent essential nutrients and are critical components of most fertilizers. In this context, tremendous opportunities of biorefinery-based valorization of sewage sludge could be explored taking into account this promising feedstock. Also, to prevent adverse effect on human health and environment, and to maximize of nutrient recovery, considerably more work will need to be done to determine the fate of nutrients such as nitrogen, phosphorous, and heavy metal—retention in hydrochar or leaching to LF— along the hydrothermal carbonization. Besides, further research needs to examine more closely the links between catalyzers including citric and hydrochloric acid and nutrients recovery since preliminary studies have shown interesting results concern hydrochar yield and N and P recovery.

Abbreviations

Abbreviations

AC: Activated carbon
AcoD: Anaerobic co-digestion
AD: Anaerobic digestion
BET: Brunauer–Emmett–Teller
BMP: Biochemical methane potential
COD: Chemical oxygen demand
DWAS: Dewatered waste activated sludge
FAN: Free ammonia nitrogen
FAS: Ferrous ammonium sulfate
FID: Flame ionization detector
GC: Gas chromatography
HHV: Higher heating value
HTC: Hydrothermal carbonization
IC: Inorganic carbon
LF:Liquid fraction from hydrothermal carbonization
PA: Partial alkalinity
PSS: Primary sewage sludge
PW: Process water
SEM: Scanning electron microscopy
SS: Sewage sludge
TA: Total alkalinity
TA: Total ammonia
TAN: Total ammonia nitrogen
TC: Total carbon
TIC: Total inorganic carbon
TKN:Total Kjeldahl nitrogen
TN: Total nitrogen
TOC: Total organic carbon
TS: Total solids
TSS: Total suspend solids
VFA: Volatile fatty acid
VS: Volatile suspend solids
VSS: Volatile suspend solids
WAS: Waste activated sludge